The ocean-atmosphere cycles of methyl halide trace gases in the Southern Ocean and Tasmanian coastal waters

Michael Grose

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Michael Grose
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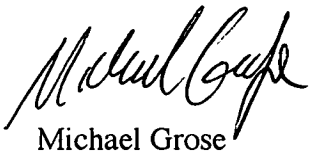

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Abstract

The trace gases methyl bromide and methyl iodide are important vectors for the transport of halogens from the ocean to the atmosphere. The halogens play roles in atmospheric reactions including catalytic ozone destruction and iodine has a role in the formation of new particles. The oceans are a large source and sink of the methyl halide gases and there are known biological and photochemical sources in the surface ocean. However the ocean-atmosphere cycle and the variables controlling production are still quite poorly understood. This study investigates the marine sources and sinks of marine methyl halides, particularly the biogenic source in the open ocean, coastal and inshore waters, in the region of the Cape Grim Baseline Air Pollution Station, Tasmania, in the period 2003 to 2007.

Methyl halide concentrations measured at Cape Grim under the Advanced Global Atmospheric Gas Experiment are made under all conditions, but this study focuses on the measurements made in baseline air that originates over the Southern Ocean and has no contact with land for some time prior to reaching Cape Grim. Methyl bromide in baseline air in 2004-2005 showed a mean concentration of 7.27 pptv, with very minor seasonal changes with no evidence of a strong daily cycle. In contrast, methyl iodide concentration in baseline air in 2004-2006 showed a seasonal cycle with a maximum of 1.62 pptv in late summer to autumn and a minimum of 0.87 pptv in late winter to spring, and was correlated with sea surface temperature and to primary production in the adjacent ocean, with a time offset. This was consistent with a source from both photochemical production and biological production, together with temperature-dependent chemical loss and flux processes. The methyl iodide record also showed increased frequency and magnitude of short-term peaks over summer, consistent with local sources from coastal waters. There was also a distinct daily cycle consistent with the atmospheric photochemical sink.

The concentrations of methyl halides in seawater and air were measured in the waters off Cape Grim using gas chromatography with electron capture detection. Seawater concentration and sea-air saturation of methyl halides were typical of temperate waters, with a pattern of higher magnitude and variability closer to the

shore. An exponential decrease in concentration with distance from the coast out to 5 km was observed, then a further decrease out across the continental shelf and into the open ocean. Mean methyl bromide seawater concentration from all measurements was 30 pM inshore, 7 pM at 5 km, 4 pM in shelf waters and 1.5 pM in open ocean. Mean methyl iodide seawater concentration was 44 pM at the shore, 11 pM at 5 km, 2 pM in shelf waters and 0.7 pM in open ocean. This created a strong source region in coastal waters with consistent positive saturations, falling to a minor source or sink in the open ocean. Open ocean methyl iodide concentration showed a positive relationship with inorganic iodide, suggesting a positive or synergistic relationship. Production of methyl halides in coastal waters showed some correlations to phytoplankton numbers during high biomass events, including a bloom of diatoms of the genus *Chaetoceros*.

Methyl halide concentrations were higher and more variable in inshore waters near beds of bull kelp (*Durvillaea potatorum*), and one period of high methyl iodide saturation at the coast in summer was followed by detection of a peak in ultra-fine condensation nuclei at the station. It is unlikely the methyl iodide acted as a precursor to new particle formation in this instance, but this observation suggests that the peak in methyl iodide was concurrent with an emission of other precursor gases or particles directly from kelp. Bull kelp emits moderate amounts of iodine gas (18.1 pmol g^{-1} min^{-1}, using fresh weight of kelp) when exposed to the air and under photo-oxidative stress, and this is also unlikely to act as a precursor to new particle formation. Chamber experiments showed that particles formed above kelp under photo-oxidative stress consisted of aromatic organic compounds. It appears likely that the role of iodine in particle formation processes is not as significant as at other locations such as Mace Head, Ireland, but emissions of an unknown and possibly organic precursor gas from kelp is likely to contribute new particles at Cape Grim.

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Chapter 1. Introduction and literature review

1.1 Environmental context

The oceans and atmosphere can be thought of as a single coupled system rather than two separate entities. In fact, the atmosphere, hydrosphere, lithosphere, cryosphere and biosphere all interact and are interlinked to form the Earth system.

There is a close interaction between ocean and atmosphere that fundamentally determines the functioning of both. Physical, chemical and biological processes are intimately involved in this interaction. Figure 1.1 shows a schematic illustrating some of the major interactions between the ocean and atmosphere. These include heat, light, kinetic energy (wind driven currents, waves, swells), solid material, dust, water vapour, sea salt and aerosol.

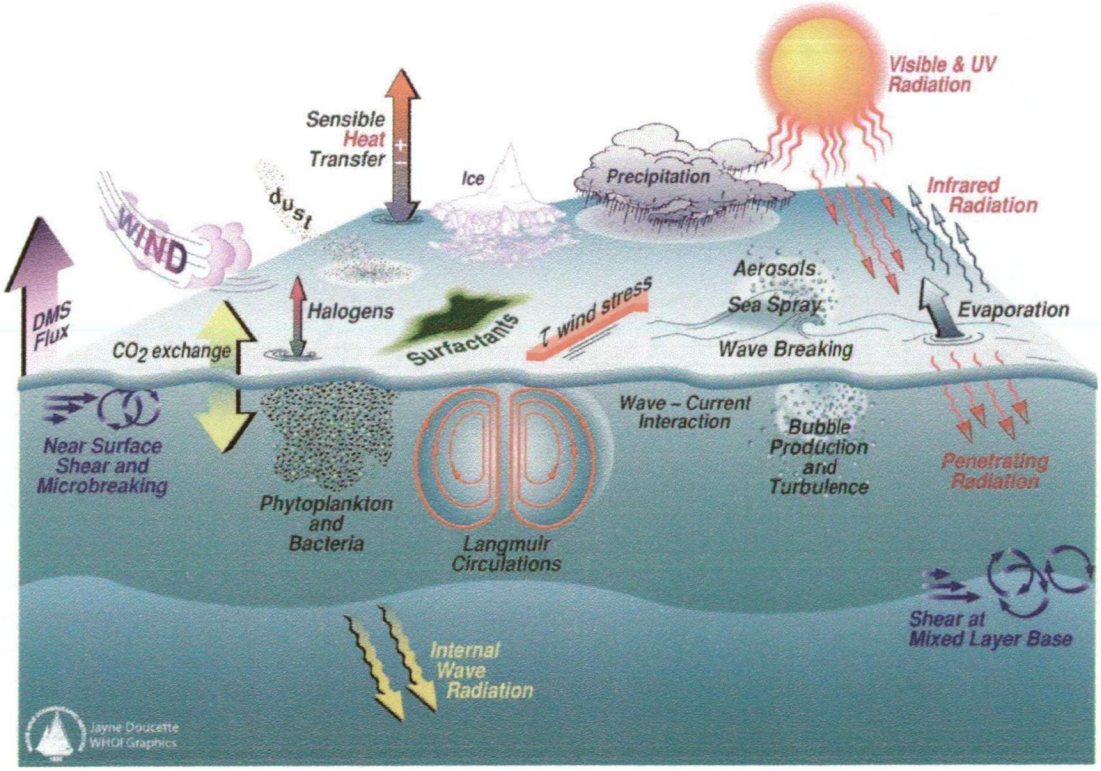

Figure 1.1 Major interactions between ocean and atmosphere (source: Surface Ocean Lower Atmosphere Study (SOLAS) research partnership)

There is continual and important gas transfer between the ocean and atmosphere across the air-sea boundary. Carbon dioxide and oxygen move across the air-sea boundary, linking the atmospheric and marine cycles of these gases. Of interest here is the transfer of trace gases between the ocean and atmosphere, which represents an important link in their global cycles and play important roles in the atmosphere.

1.1.1 Earth's atmosphere

The Earth's atmosphere consists of several defined layers (Figure 1.2). The troposphere occurs from the earth's surface up to 6 to 20 km in altitude. It is split at the equator due to the overturning circulation of the Hadley cells, so the transfer of atmospheric gases within the troposphere is restricted across the equator. The stratosphere lies from the top of the troposphere up to approximately 50 km. The boundary between these two layers is named the tropopause. Above the stratosphere lies the mesosphere at approximately 50 to 85 km altitude, the thermosphere at 85 to 690 km, and the exosphere at 690 to 10,000 km. Within the thermosphere lies the ionosphere, the layer in which gas can be ionized by solar radiation. The majority of the gas in the atmosphere is concentrated in the lower layers; 50% lies below 5.6 km altitude, 90% lies below 16 km and 99.99997% lies below 100 km (named the Kármán Line).

There is a boundary layer directly above the Earth's surface, defined as the air layer affected by diurnal heat, moisture or momentum transfer to or from the surface. The general name for this layer is the planetary boundary layer; over the sea surface it is named the marine boundary layer (MBL) and is typically in the order of 0.5 – 2 km thick, depending on heat, wind, turbulence and other factors.

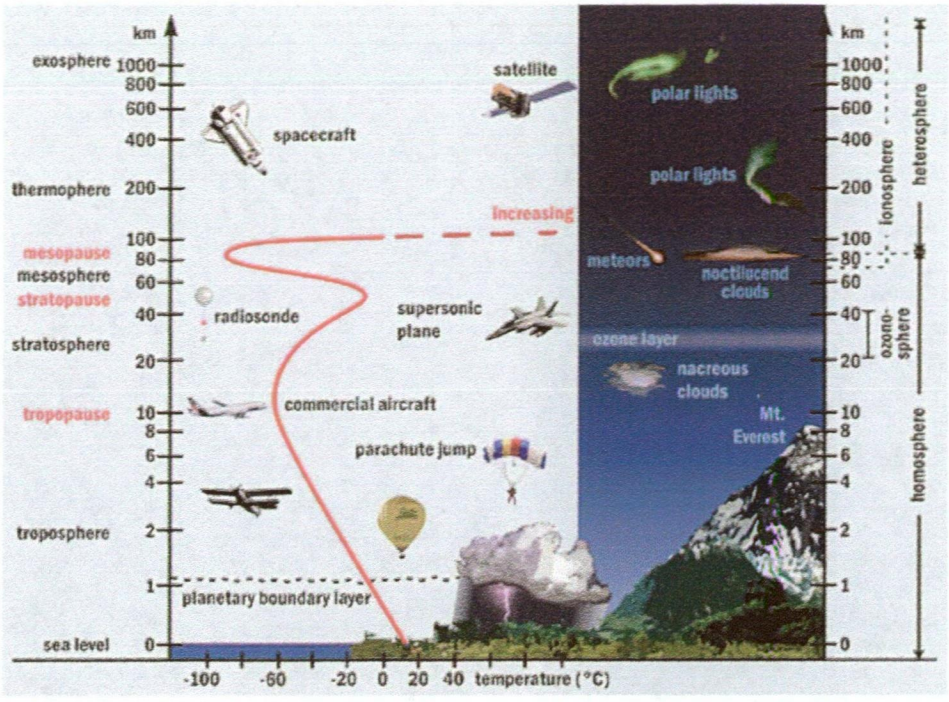

Figure 1.2 The vertical structure of the Earth's atmosphere showing the defined layers, human activities and natural phenomena found with altitude (source: Kowoma 2007)

The atmosphere is a critical component of the Earth system, and the composition of gases in the atmosphere has important effects on climate. Air is made up of mainly nitrogen and oxygen, with other gases making up less than 2% of the composition (Table 1.1). All other components in the atmosphere are known as trace gases, defined as less than 1% of the Earth's atmosphere. Trace gases play important roles in the atmosphere, and their significance is greater than their low concentrations may suggest. The focus of this study is the trace gases methyl bromide (CH_3Br) and methyl iodide (CH_3I). These gases have a significant role in processes of ozone depletion in the troposphere and stratosphere and a monor role in radiative forcing (the greenhouse effect). Methyl iodide may also have a role as a precursor gas to the formation of new particles.

Table 1.1 Composition of the major gases in the Earth's atmosphere, also indicated are some trace gases with important effects on climate processes (solid particles not included in this analysis, ppm = parts per million molar, climatic effects are RF = radiative forcing, OD = ozone depletion, P = precursor to particle formation)

Component	Chemical Symbol	Composition (%)	Composition (ppm)	Climate Effects
Major gases				
Nitrogen	N	78.08	780,840	
Oxygen	O_2	20.95	209,460	
Water vapour	H_2O	~1	~10,000	RF
Trace gases				
Argon	Ar	<1%	9,340	
Carbon dioxide	CO_2		383	RF
Neon	Ne		18.18	
Helium	He		5.24	
Methane	CH_4		1.745	RF
Krypton	Kr		1.14	
Hydrogen	H_2		0.55	
Nitrous oxide	N_2O		0.32	RF, OD
Carbon monoxide	CO		0.1 - 20	RF
Ammonia	NH_3		0 - 0.5	
Xenon	Xe		0.09	
Ozone	O_3		0 - 0.07	
Nitrogen dioxide	NO_2		0.02	
Iodine	I_2		0.01	P
Sulfur dioxide	SO_2		0.001 - 0.1	
Nitric oxide	NO		0.001	
CFC-12	CF_2Cl_2		0.00055	OD
CFC-11	$CFCl_3$		0.00025	OD
Dimethyl sulfide	C_2H_6S		0.0005	OD, P
Methyl bromide	CH_3Br		0.00001	RF, OD
Methyl iodide	CH_3I		0.000002	OD, P

1.1.2 Climatic relevance of bromine

Methyl bromide enters the atmosphere from various sources and has important effects on the climate system. It is eventually broken down to inorganic bromine forms, which also have important effects in atmospheric processes. In this way, the emission of methyl bromide is a transport vector of bromine to the atmosphere.

Ozone depletion

The three main catalytic cycles involving the reactions of inorganic bromine result in a net reaction of two ozone molecules to form three oxygen molecules (see Equations 1.1a – 1.3e).

	$Br + O_3$	→	$BrO + O_2$	1.1a
	$BrO + HO_2$	→	$HOBr + O_2$	1.1b
	$HOBr + h\nu$	→	$OH + Br$	1.1c
	$OH + O_3$	→	$HO_2 + O_2$	1.1d
Net	$2\ O_3$	→	$3\ O_2$	
	$Br + O_3$	→	$BrO + O_2$	1.2a
	$BrO + ClO$	→	$Br + Cl + O_2$	1.2b
	$Cl + O_3$	→	$ClO + O_2$	1.2c
Net	$2\ O_3$	→	$3\ O_2$	
	$Br + O_3$	→	$BrO + O_2$	1.3a
	$BrO + NO_2 + M$	→	$BrONO_2 + M$	1.3b
	$BrONO_2 + h\nu$	→	$Br + NO_3$	1.3c
	$NO_3 + h\nu$	→	$NO + O_2$	1.3d
	$NO + O_3$	→	$NO_2 + O_2$	1.3e
Net	$2\ O_3$	→	$3\ O_2$	

Bromine gases are important contributors to ozone depletion chemistry in the lower stratosphere, responsible for approximately 10-20% of the total ozone loss rate in the mid to low latitude (Brasseur *et al.* 1999). Bromine is more efficient at depleting ozone than is chlorine by a factor of 40-100, depending on latitude and altitude (Penkett *et al.* 1995, Kurylo *et al.* 1998). The Ozone Depletion Potential (ODP) of a gas is a measure of its ability to deplete ozone relative to the reference compound CFC-11 on a mass emitted basis, and can be defined as a steady-state (over unlimited time) or time-dependant (over a specific time horizon), from models or semi-empirical data (Penkett *et al.* 1995). The ODP for methyl bromide has been

calculated as 0.4 (Schauffler *et al.* 1999). The ODP of other bromine-containing gases include 7-12 for halons (Schauffler *et al.* 1999), 0.1 for CH_2ClBr and 0.03 for *n*-propyl bromide (Wuebbles *et al.* 1999). The concentrations of many anthropogenic ozone-depleting gases increased during the twentieth century and are now in decline after controls were implemented under the Montreal Protocol. A summary of the contribution of various gases to ozone depletion in the atmosphere since 1936 is shown in Figure 1.3.

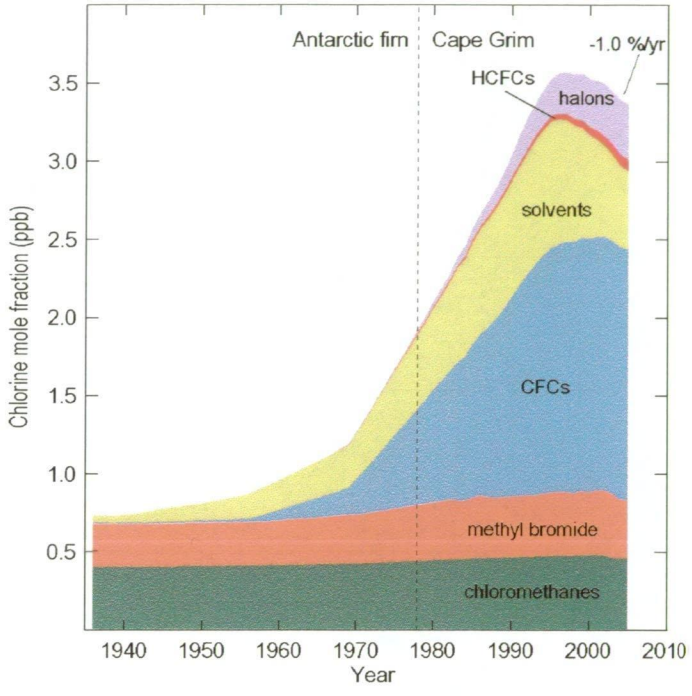

Figure 1.3 Mole fraction of ozone depleting substances in baseline air at Cape Grim and in air trapped in Antarctic compressed snow (firn) from 1936 to 2005, all gases are converted to equivalent content of chlorine (source: Paul Fraser, CSIRO)

Radiative forcing

In addition to their ozone-depleting potential, organic bromine compounds contribute to climate warming through radiative forcing. The effectiveness of a greenhouse gas is expressed as its global warming potential (GWP), and is calculated in comparison to the reference compound CO_2 on a mass emitted basis, over a particular time horizon (Kurylo *et al.* 1998). Carbon dioxide has an effective atmospheric lifetime of tens of thousands of years (Archer 2005). Methyl bromide has a lifetime of 0.7 years and a radiative efficiency of 0.01 W m^{-2} ppb^{-1}, giving it a GWP of 17 over 20 years, 5 over 100 years and 1 over 500 years (Forster *et al.* 2007). For comparison, the GWP

of methane is 72 over 20 years, 25 over 100 years and 7.6 over 500 years (Forster *et al.* 2007).

1.1.3 Climatic relevance of iodine

Methyl iodide has important effects in the atmosphere and is a transport vector of inorganic iodine to the atmosphere, which also has important effects in atmospheric processes.

Oxidizing effects & ozone depletion

Iodine is important in the chemistry of the lower troposphere, particularly the MBL. Laboratory studies have demonstrated that iodine has an effect on the oxidizing capacity of the MBL through various cycles. The cycles of IO, HOI and OIO, can alter the partitioning of NO_X (NO_2/NO) and HO_X (HO_2, OH) (Bloss *et al.* 2005). Iodine can activate chlorine and bromine from sea-salt aerosol (McFiggans *et al.* 2002). Iodine monoxide (IO) oxidises dimethyl sulfide (DMS) to form DMS oxide (DMSO + I), although a laboratory study has indicated that this process is of minor importance under typical IO concentrations (Gravestock *et al.* 2005). Iodine also plays a role in ozone and mercury depletion episodes in the Arctic polar spring (Calvert & Lindberg 2004a,b). Iodine also participates in the catalytic destruction of tropospheric ozone through cycles similar to the other halogens.

Particle formation

Recently there has been considerable interest in the role of iodine in the processes of particle formation and growth in the MBL (O'Dowd *et al.* 2002b). Aerosols have an important effect on the radiative forcing budget of the earth through direct scattering of light and indirectly through the seeding of cloud droplet formation. Changes to the particle formation budget alter climate through primary and secondary aerosol effects. The biological emission of gases that act as precursors to particle formation may create a feedback loop between ocean and atmosphere with a homeostatic effect. A more detailed description of these processes is outlined in Section 1.9

1.2 Aims and scope of this study

This study contributes to the understanding of the ocean-atmosphere cycle of the methyl halide gases methyl bromide and methyl iodide in the Cape Grim Baseline Air Pollution upwind fetch zone of the Southern Ocean. Air from this Southern Ocean marine zone is termed 'baseline', sources and sinks from other sectors will not be considered here (a discussion of 'baseline' is found in Chapter 2.2.6).

Two main approaches were taken to pursue this goal: the analysis of time series data from the Cape Grim station and field measurements. The time series data of methyl halides from the Cape Grim station was used to place the field measurements in context and provide information on the seasonal cycles and other temporal changes in concentration. Links between the temporal changes in concentration and physical and biological characteristics of the ocean were examined. The field measurements were in three main regions within the upwind fetch zone of the Cape Grim station: the Southern Ocean south of Australia, coastal waters of northwest Tasmania (5-10 km offshore) and the coast adjacent to the station (< 5 km offshore, Figure 1.4).

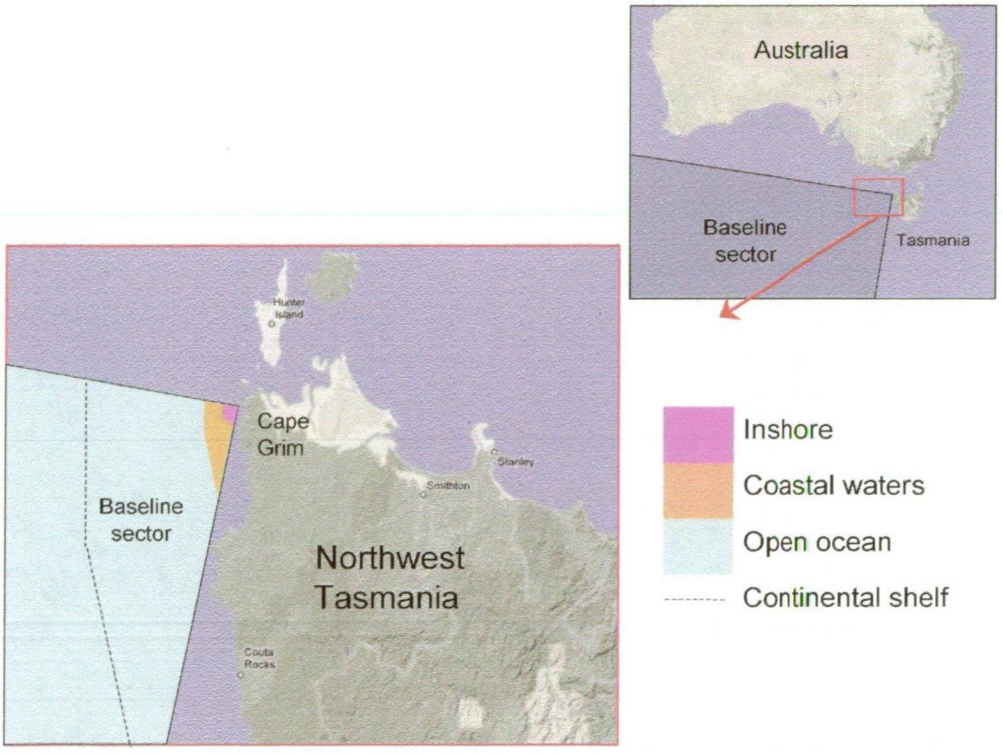

Figure 1.4 Map of the Southern Ocean west of Tasmania, indicating the Cape Grim baseline sector and the regions of ocean of interest in this study

The collection of field data was limited by access to boats, weather conditions and budget, so a limited sampling regime is used to address a few specific questions. The sign and magnitude of methyl halide saturation in the open ocean south of Australia was estimated. Also in the open ocean, the relationships between methyl halides, temperature and phytoplankton biomass and between inorganic iodide (I^-) and methyl iodide concentrations were examined. The seasonality of the ocean source of methyl halides in coastal waters off northwest Tasmania was assessed, and any incidents of elevated methyl halide production during phytoplankton blooms were examined. The magnitude and variability of the source of methyl halides from the inshore waters and from kelp beds at the coast was measured, including a calculation of any enrichment in this region. Links between the emissions of methyl iodide, iodine (I_2) and other compounds from coastal kelp beds and events of new particle formation were examined.

1.3 Environmental chemistry of methyl bromide

Methyl bromide is a colourless gas at room temperature (b.p 4.5 °C) with a slightly sweet odour. It has the formula CH_3Br. It is also known as bromomethane or monobromomethane; it will be referred to as methyl bromide in this study to be consistent with the general literature. From recent estimates it is thought that the total concentration of organic bromine in the atmosphere is 20 pptv (parts per trillion by volume) and the total flux of organic bromine to the atmosphere is 500 Gg yr^{-1} (gigagrams per year) (Orlando 2003). Methyl bromide is the major component of this organic bromine and is thought to constitute half of the organic bromine present in the atmosphere with a global average concentration of approximately 10 pptv (Butler 2000, Kurylo *et al.* 1998).

Methyl bromide and other organic brominated gases from marine and terrestrial sources are a transport vector of bromine to the atmosphere, where they undergo conversion to inorganic forms. There is some destruction of methyl bromide in the troposphere, but the mixing ratio of 15 to 20 pptv of organic bromine can be present up to the tropause (Orlando 2003). More rapid destruction occurs when it reaches the lower stratosphere and complete destruction of all organic forms of bromine in the

stratosphere occurs within five years (Wamsley *et al.* 1998). The products of this destruction are inorganic bromine species such as BrO, HOBr, $BrONO_2$.

1.3.1 Historic trends

Measurements of air in ice cores and firn (compressed snow) from various sites in Antarctica have been used to assess the past atmospheric levels of methyl bromide. There was no significant trend in methyl bromide from 160 BC to 1860 AD (Saltzman *et al.* 2008). There was a gradual rise in methyl bromide concentration over the first part of the 20th century, followed by a rapid increase in the 1970s and 1980s of 0.05-0.06 pptv yr^{-1} leading to at least a 2 pptv increase in methyl bromide abundance in the last half of the 20th century (Butler *et al.* 1999, Sturges *et al.* 2001). Direct measurements of methyl bromide in air were first made by Singh *et al.* (1977), and a continuing regime of measurement occurs in many places. Continuous measurement of methyl bromide at Cape Grim has been made since 1998 under the Advanced Global Atmospheric Gases Experiment (AGAGE) program (e.g. Cox *et al.* 2005; Simmonds *et al.* 2004). The AGAGE continuous records and an analysis of the 30-year 'air archive' since 1977, and the firn air are shown in Figure 1.5, showing the mid 20th Century increase and the recent downward trend.

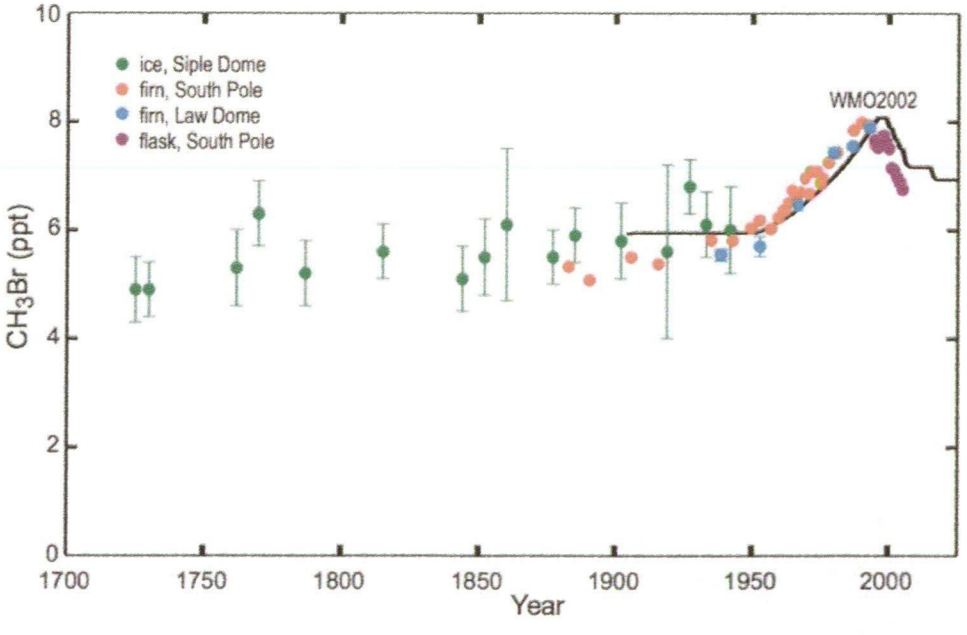

Figure 1.5 History of methyl bromide abundance in the southern polar atmosphere from Antarctic ice, firn and flask measurements, WMO 2006 (orange Butler *et al.* (1999), blue Trudinger *et al.* (2004), green Saltzman *et al.* (2004), purple Montzka *et al.* (2003), black line emission scenario Ab from WMO 2002 (Montzka *et al.* 2003))

1.3.2 Global distribution

Measurements of methyl bromide have been made over a wide geographic range, allowing an analysis of global distribution (e.g. Andreae *et al.* 1996, Berg *et al.* 1984, Blake *et al.* 1996a, b, c, Blake *et al.* 1997, Carpenter *et al.* 1999, Cicerone *et al.* 1988, Fabian *et al.* 1981, Groszko & Moore 1998, Khalil & Rasmussen 1985, Khalil *et al.* 1993, King *et al.* 2000, Kourtidis *et al.* 1998, Lal *et al.* 1994, Lobert *et al.* 1995, Lobert *et al.* 1997, Manö & Andreae 1994, Moore & Webb 1996, Penkett *et al.* 1985, Pfeilsticker *et al.* 2000, Rasmussen & Khalil 1984, Schauffler *et al.* 1999, Schauffler *et al.* 1998, Schauffler *et al.* 1993, Singh & Kanakidou 1993, Singh *et al.* 1983, Wingenter *et al.* 1998, Yokouchi *et al.* 2000, Cox 2001, Cox *et al.* 2005). In a review, Orlando (2003) assessed the global average concentration of methyl bromide in air to be approximately 10 pptv, with concentrations higher in the northern hemisphere (about 11.5 pptv) and lower in the southern hemisphere (about 9 pptv), a difference of 15-35%. Measurements made by Yokouchi *et al.* (2000) along the western Pacific rim illustrated the hemispheric gradient (Figure 1.6). This difference implies greater source strength in the northern hemisphere (around 40 Gg yr^{-1}; Wingenter *et al.* 1998), and a restricted transfer betwen the northern and southern hemisphere air masses. There is a measured seasonal cycle of atmospheric methyl bromide, in the northern hemisphere, with concentrations of 10.5 to 11 pptv in March-April and 9.5 to10 pptv in September, but not in the southern hemisphere (Wingenter *et al.* 1998, Cox *et al.* 2005). Therefore, the inter-hemispheric ratio varies from 1.35 in March-April, to 1.1 in September (Wingenter *et al.* 1998). The present concentrations and ratios may be different to these values due to the downward trend in anthropogenic sources mentioned above.

Because methyl bromide is a relatively long-lived atmospheric component (around 0.7 years), altitude gradients within the troposphere are weak (Blake *et al.* 1997, Fabian *et al.* 1981, Kourtidis *et al.* 1998, Lal *et al.* 1994, Schauffler *et al.* 1999, Schauffler *et al.* 1998, Schauffler *et al.* 1993). In the stratosphere there is a major reduction in methyl bromide concentration due to destruction via chemical reactions, including with ozone. Early balloon measurements (Fabian *et al.* 1981, Lal *et al.* 1994) and more recent studies (Blake *et al.* 1997, Kourtidis *et al.* 1998, Schauffler *et al.* 1999, Schauffler *et al.* 1998) support this view of weak or negligible gradients of

methyl bromide up to the tropause, and then a sharp decrease in the lower stratosphere.

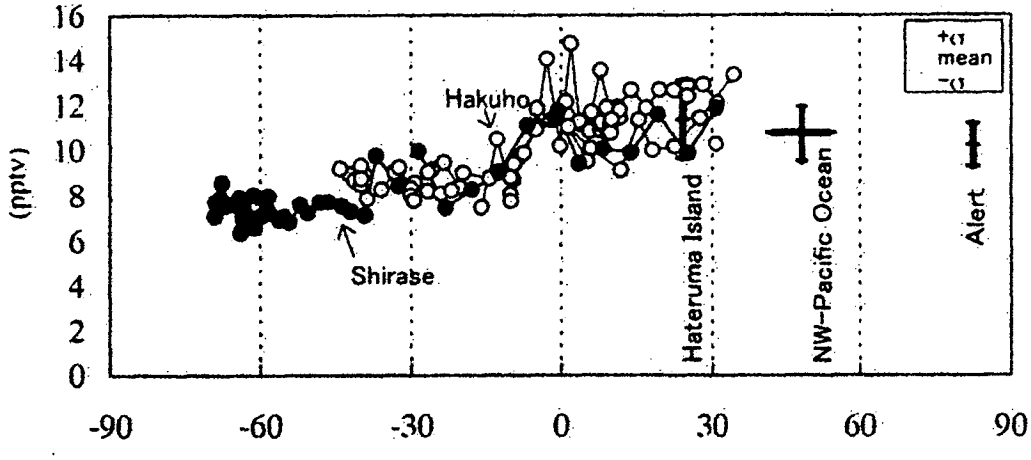

Figure 1.6 Measurements of atmospheric concentration of methyl bromide made along the western Pacific rim, showing a hemispheric gradient in concentration (source: Yokouchi *et al.* 2000)

1.3.3 Sources

The sources of methyl bromide fall into two categories: anthropogenic and natural. The three known anthropogenic sources of methyl bromide are fumigation, biomass burning and leaded petrol; the four known natural sources are wood-rotting fungi, wetland ecosystems, higher plants and the oceans (Orlando 2003). There may be other sources of methyl bromide that are presently unknown.

Anthropogenic sources caused an increase in global methyl bromide concentration in the mid 20th century and are now in decline since the control of anthropogenic emission (shown in Figure 1.5). However, the sources of methyl bromide have been estimated to provide ~125 Gg yr^{-1}, and the sinks have been measured at ~ 200 Gg yr^{-1}, a difference of 75 Gg yr^{-1} (Kurylo *et al.* 1998). This indicates that the sources and sinks have not been fully assessed yet, and the budget is not fully closed. A summary of all the known sources and sinks is found in Table 1.2, including rate factors used in the assessment by WMO in 2002 (Montzka & Fraser 2002).

Table 1.2 Sources, sinks and atmospheric lifetime for methyl bromide

Source or Sink Type	Source or Sink Strength (Gg yr^{-1})		Atmospheric Lifetime (year)
	Mean	Range	
Sources			
Fumigation	40.8	28.2 to 64.4	
Gasoline	5	0 to 10	
Biomass Burning	20	10 to 40	
Vegetation etc.	30.3	15.7 to 59.6	
Oceans	63	23 to 119	
Subtotal	159	77 to 293	
Sinks			
Atmos. Reactions	-80	-60 to -100	1.7
Soils	-47	-32 to -154	3.4
Plants	?		?
Oceans	-77	-37 to -133	1.9
Subtotal	-204	-129 to -387	
Total	-45	-220 to +71	0.7

Adapted from: WMO 2002, Chapter 1 (Montzka & Fraser 2002). This table is generated from various sources noted therein. The table is not updated in the WMO 2006 report.

The quantity of methyl bromide used for fumigation (mainly of soils but also durables, perishables and structures) increased from 45 Gg in 1984 to 71.6 Gg in 1992, and is now in decline (Penkett *et al.* 1995, Singh & Fabian 1999). Not all of the methyl bromide used in these processes enters the atmosphere; between 25 and 75% of the methyl bromide used in soils is released to the atmosphere, depending on the characteristics of the process (Williams *et al.* 1999). Similarly, only 70% of that used on durables is released to the atmosphere, but 100% of that used on structures is released (Kurylo *et al.* 1998).

Burning of various types of natural biomass including grasses and forest produces methyl bromide, and an appraisal of available data suggested a global source of approximately 20 Gg yr^{-1} in the mid nineties (Kurylo *et al.* 1998). In the early 1970s, organic bromine compounds in leaded petrol represented an estimated emission of methyl bromide of 43 Gg yr^{-1}, which fell to 5 Gg yr^{-1} in 1995 (Thomas *et al.* 1997), and is likely to be even lower at the present time.

Wood-rotting fungi produce methyl bromide in the process of litter decomposition, representing a global source of around 1.7 Gg yr^{-1} (Lee Taylor & Holland 2000). Wetlands and the associated ecosystems are a source of methyl bromide, including around 1.3 Gg yr^{-1} from rice paddies (Redeker *et al.* 2000), 0.9 Gg yr^{-1} from peat-lands and 5 Gg yr^{-1} from wetlands (Dimmer *et al.* 2001). There is also a source of methyl bromide from salt marshes, which has ben estimated as up to 14 Gg yr^{-1} (Rhew *et al.* 2000, Rhew *et al.* 2002, Bill *et al.* 2002), however other studies have calculated a much lower estimate (Cox et al. 2004, Dimmer et al. 2001) . Certain higher vascular plants are methyl bromide sources, including cabbage and rapeseed (Attieh *et al.* 1995, Saini *et al.* 1995, Gan *et al.* 1998). Shrub-land vegetation can represent a source (Rhew *et al.* 2001), but herbaceous, deciduous and coniferous vegetation can be a significant sink of methyl bromide (Jeffers *et al.* 1998). There are significant sources from coastal-terrestrial and/or coastal-seawater regions in Tasmania and southeastern Australia detected at Cape Grim (Cox *et al.* 2003).

Freshwater lakes and streams are a minor source of methyl bromide (< 0.5 % of global source) that shows a seasonal cycle with consistent super-saturation in summer and strong under-saturation in winter (Huang *et al.* 2000). This seasonal cycle has been attributed to natural physical (gas exchange) and biological (phytoplankton, bacteria) processes.

Cox (2001) studied the regional sources and sinks of halomethanes around Cape Grim. Trajectory analyses identified coastal-terrestrial and coastal-seawater areas as well as the Port Philip Bay industrial area as major source regions of methyl bromide. Direct measurements of methyl bromide fluxes from vegetation using flux chambers showed coastal wetlands were the only significant source of methyl bromide, *Melaleuca* and *Eucalyptus* forests were a minor sink, and tussock & pasture were variously a sink and a source.

The oceans represent both a major source and sink of methyl bromide, and will be discussed in a separate section (Chapter 1.5).

1.3.4 Sinks

The three major natural sinks of methyl bromide are atmospheric reactions, soil bacteria and the oceans, with a possible sink from various vegetation types. There are no anthropogenic sinks of methyl bromide.

The atmospheric reactions of methyl bromide that represent a sink are: reactions with hydroxyl radicals (generally $OH^{\cdot} + CH_3Br \rightarrow CH_2Br^{\cdot} + H_2O$), reactions with other atmospheric oxidants (such as $Cl^{\cdot}$, O_3 & NO_3), and photolysis (Orlando 2003). The major loss is through reaction with hydroxyl; the partial lifetime for methyl bromide in this process is 1.7 years (Kurylo *et al.* 1998).

The magnitude of the soil sink is still uncertain due to different estimates in the contribution of cultivated soils. The global contribution by cultivated soils has variously been estimated to be 2.7 Gg yr^{-1} (Shorter *et al.* 1995), 7.5 Gg yr^{-1} (Varner *et al.* 1999) and 66 Gg yr^{-1} (Serça *et al.* 1998). The estimates for the total soil sink (cultivated and natural soils) are 140 (±70) Gg yr^{-1} (Serça *et al.* 1998) and 42 Gg yr^{-1} (Shorter *et al.* 1995). The World Meteorological Organization (Kurylo *et al.* 1998) adopted the latter estimate.

1.4 Environmental chemistry of methyl iodide

Iodine (from the Greek *iodes* meaning 'violet') has the atomic number 53. It was discovered by Courtois in 1811, and exists as a bluish-black lustrous solid, volatilzing at ordinary temperatures into a blue-violet gas of I_2. Iodine forms compounds readily with many elements but is less reactive than other halogens, which displace it from organic iodides. Methyl iodide (CH_3I) is also known as iodomethane. It is a dense, colourless, volatile liquid with an acrid odour at room temperature (-66.5 °C melting point, 42.4 °C boiling point). For consistency with the general literature, it will be referred to as methyl iodide in this study.

Lovelock *et al.* (1973) was the first to measure organic iodine gases in the atmosphere. The iodine-containing organic compounds found in the ocean and atmosphere include methyl iodide, higher alkyl iodides and multiply halogenated methanes (CH_2I_2, CH_2ICl etc.). Methyl iodide represents around 60% of the organic iodine in the atmosphere (Carpenter *et al.* 1999) is the most abundant form of atmospheric iodine.

1.4.1 Environmental cycling of iodine

The largest reservoir of iodine is in the oceans, and the most stable form of iodine in seawater is iodate (IO_3^-). Reduction of iodate to iodide occurs in the surface layer of the ocean via physical, chemical and biological pathways. Iodine is volatilized from the ocean to the atmosphere through various pathways including the formation of organic iodine gases such as methyl iodide. Organic iodine gases generally have a short lifespan in the atmosphere where they are quickly broken down into I^- by various mechanisms. Iodine is deposited onto land by wet and dry precipitation, where it is an essential micronutrient in many organisms in the terrestrial biosphere. For humans iodine is an important component of the thyroid hormone thyroxine. Insufficient intake leads to a group of diseases known as Iodine Deficiency Disorders (IDD), including goitre. Further details on the cycling of iodine in the environment can be found in Appendix D, which is a copy of the book chapter Butler *et al.* (2007).

1.4.2 Sources

Methyl iodide has an atmospheric lifetime of only a few days and so transport over long distances is not possible. For this reason, observations of elevated methyl iodide levels (tens of pptv) are typically found near areas of high source activity such as high ocean productivity or biomass burning. There appears to be no clear long-term temporal trends in methyl iodide in firn air from Antarctica (Sturges *et al.* 2001).

The major sources of methyl iodide are natural, but there is still considerable doubt regarding the relative strength of the different sources. It has been thought for a long time that the largest natural source is oceanic emissions (Vogt 1999), with few emissions from terrestrial sources. However, a recent synthesis of data from research

flights, long-term ground-observing network and a field campaign has identified a large terrestrial source of methyl iodide (Sive *et al.* 2007). There are emissions of 2,700 ng m^{-2} d^{-1} from mid-latitude vegetation and soils, similar values to oceanic emission, contributing 33 Gg yr^{-1} to the global budget (Sive *et al.* 2007). Oceanic sources are discussed in a Chapter 1.5.

There are also anthropogenic sources, the most significant being rice paddies, emitting 70 Gg yr^{-1}, as much as 30% of the total source (Redeker *et al.* 2000). Biomass burning has been measured to be a small but significant source of methyl iodide (Andreae *et al.* 1996, Blake *et al.* 1996c, Carpenter *et al.* 1999), contributing up to 14 Gg yr^{-1} (Andreae & Merlet 2001). Fossil fuel burning contributes a negligible amount to the methyl iodide budget (Chameides & Davis 1980).

Early reports of elevated methyl iodide in urban areas (Lillian *et al.* 1975) were not supported by subsequent measurements (Rasmussen *et al.* 1982b, Singh *et al.* 1983). Potential anthropogenic sources include as a replacement for halon fire suppressants, which could represent a source of up to 20 Gg yr^{-1} (Solomon *et al.* 1994) and as a fumigant for agriculture following the phase out of methyl bromide.

1.4.3 Sinks

Methyl iodide has a typical lifetime of 3 to 5 days, which is longer than the lifetime of CF_3I (1-2 days), CH_2ICl (a few hours), CH_2IBr (< 1 hour), and CH_2I_2 (a few minutes) (Fahr *et al.* 1995, Mössinger *et al.* 1998, Rattigan *et al.* 1997, Soloman *et al.* 1994), but much shorter than that of methyl bromide. The lifetime of methyl iodide is typically 4 to 5 days at temperate sites such as Cape Grim (Cohan *et al.* 2003). This lifetime is determined almost entirely by photolysis. Iodine-containing organic compounds undergo rapid photolysis under UV light, to produce $I^{\cdot}$ radicals and this is the largest sink of methyl iodide (Equation 1.4a-c).

Methyl iodide also reacts with $OH^{\cdot}$ radicals in the atmosphere with an estimated lifespan of 0.5 years (Equation 1.5a,b), and the removal rate by this process is negligible compared to photolysis (Brown *et al.* 1990, Garraway & Donovan 1979). The other atmospheric sink of methyl iodide is reaction with $Cl^{\cdot}$ (Equation 1.6a,b),

which is also of minimal importance for methyl iodide, affecting mainly the larger alkyl halides (Orlando 2003).

	$CH_3I + h\nu$	→	$CH_3^{\cdot} + I^{\cdot}$	(1.4a)
	$I^{\cdot} + I^{\cdot}$	→	I_2	(1.4b)
Or	$I^{\cdot} + O_3$	→	$IO + O_2$	(1.4c)
	$OH^{\cdot} + CH_3I$	→	$CH_2I^{\cdot} + H_2O$	(1.5.a)
Or	$OH^{\cdot} + CH_3I$	→	$CH_3^{\cdot} + HOI$	(1.5.b)
	$Cl^{\cdot} + CH_3I$	→	$CH_2I^{\cdot} + HCl$	(1.6.a)
Or	$Cl^{\cdot} + CH_3I$	↔	$CH_3I{\bullet}Cl$	(1.6.b)

1.5 Methyl halides and the oceans

1.5.1 Saturation

The transfer of methyl bromide and methyl iodide into and out of the oceans means they act as a major source and sink of of these gases to the atmosphere. The ocean is also a large reservoir or 'buffer' that will compensate for future changes in anthropogenic or terrestrial source strengths of methyl halides and have a regulating effect (Butler 1994).

Different areas of ocean can act as a net source or a sink of methyl halides, varying on spatial and temporal scales. The concentration of methyl halide gases in seawater can be defined using various units, in this study the unit picomolar (pM) is used, which is equivalent to picomoles per liter. The saturation of methyl halide in seawater compared to the air above determines the source or sink term of the ocean at that location. Saturation is calculated using Equation 1.7, incorporating a Henry's Law constant for the specific gas. For example, methyl bromide is soluble in seawater, with a Henry's law constant (H′) given by Equation 1.8, giving a value of 0.189 at 18 °C (De Bruyn & Saltzman 1997).

$$\text{Sat}(\%) = (C_w / (C_a \times H')) \times 100 \quad (1.7)$$

C_w = methyl halide in seawater (mol l^{-1})
C_a = methyl halide in air (atm^{-1})
H' = Henry's Law constant

$$H' \text{ (mol } l^{-1} \text{ atm}^{-1}) = \exp[-171.2 + 254.3(100/T) + 77.04\ln(T/100) + S\{0.2591 - 0.1828(T/100) + 0.03142(T/100)^2\}] \quad (1.8)$$

T = temperature in Kelvin
S = salinity

The difference in concentration between seawater and air from equilibrium (100%) is termed the 'saturation anomaly'. If methyl bromide concentration in seawater is greater than saturation compared to the air (super-saturation) then methyl bromide will move from the ocean into the atmosphere and those waters represent a net source. If the reverse is true (under-saturation) methyl bromide will move into the ocean and the water represents a net sink.

The main determinants of the flux rate between ocean and atmosphere are the concentration anomaly and also the transfer velocity (Liss & Merlivat 1986, Wanninkhof 1992), given by Equation 1.9. The transfer velocity for a gas has a cubic relationship to wind speed and incorporates a Schmidt number constant (Equation 1.10). The Schmidt number is dependant on temperature (Equation 1.11).

$$\text{Flux} = k\,\Delta C \quad (1.9)$$

k = transfer velocity
ΔC = concentration anomaly

$$k = 0.0283u^3 \times (Sc/660)^{-1/2} \quad (1.10)$$

u = wind speed at 10 metres height
Sc = Schmidt number

$$Sc = 335.6M^{1/2}(1 - 0.0065T + 0.002043T^2 - 0.000026T^3) \quad (1.11)$$

T = sea surface temperature in °C

M = molecular weight

1.5.2 Ocean source of methyl bromide

The global estimate of the methyl bromide oceanic source has been revised several times as the saturation of the different ocean regions has been quantified. The first measurements were made in various regions in the Pacific Ocean where waters were found to be super-saturated representing a net source (Khalil *et al.* 1993, Singh & Kanakidou 1993, Singh *et al.* 1983). Singh & Kanakidou (1993) estimated a global net source of 60 Gg yr^{-1} based on these super-saturations in mid-latitudes. Khalil *et al.* (1993) measured lower super-saturations in these waters, inferring a lower global net source of 35 Gg yr^{-1}. However, Lobert *et al.* (1995) then showed that most of the open eastern Pacific Ocean is under-saturated (with only coastal and upwelling regions as a source), and calculated a corresponding global net sink of –13 Gg yr^{-1}.

Colder high-latitude waters were not considered in these early calculations and were hypothesized to be a source of methyl bromide, since chemical loss is much slower in cold waters (Anbar *et al.* 1996, Pilinis *et al.* 1996). However, waters in both the Arctic (Moore & Webb 1996) and Antarctic (Lobert *et al.* 1997) were measured to be under-saturated. Lobert *et al.* (1997) estimated the corresponding global net sink to be -21 Gg yr^{-1}. This under-saturation in high latitude waters implies a large biological contribution to the oceanic destruction rate (Connell *et al.* 1997, Goodwin *et al.* 1997, King & Saltzman 1997, Tokarczyk *et al.* 2001, Tokarczyk & Saltzman 2001).

A seasonal cycle in methyl bromide saturation levels was found in a systematic study in the shallow, semi-enclosed North Sea (Baker *et al.* 1999). King *et al.* (2000) subsequently found that a seasonal cycle of saturation occurs in temperate regions of the northeast Atlantic Ocean, with super-saturation in spring. An overall global sink of -16 Gg yr^{-1} was suggested, incorporating this seasonal cycle. However, Sturrock *et al.* (2003) suggests it is possible that inter-annual variability may be part of the cause for this apparent seasonal cycle, since the study was not conducted continuously over a single year. A super-saturation and net positive exchange of methyl bromide were also found inside a warm-core eddy in the North Atlantic Ocean (Yvon-Lewis *et al.* 2002).

There have been very few measurements of methyl bromide concentration or saturation in the waters near Cape Grim, or near Australia. In the Southern Ocean south of Tasmania (between 45-65°S, 144-139°E), seawater concentrations of methyl bromide were found to be within the range 0.5 to 2 pM, and saturation was 39 ± 11% below equilibrium, which reduced to around 82% below equilibrium near the Antarctic coast due to enhanced vertical mixing, indicating a net sink (Yvon-Lewis *et al.* 2004). Two measurements of methyl bromide concentration in open ocean water 80 km offshore from Couta Rocks made in March 2001 and January 2002 were 2.1 and 8.1 pM respectively, with no estimate of saturation made (Sturrock *et al.* 2003). These concentrations are similar to the maximum and minimum concentrations measured across the open ocean of the north Atlantic (2 to 8 pM, Baker *et al.* 1999). The lower value is also similar to the maximum found in the open Southern Ocean measurements further south (0.5 to 2 pM, Yvon-Lewis *et al.* 2002). Measurements of methyl bromide in coastal waters near Cape Grim were reported in Corno *et al.* (2004), which is discussed in further sections and chapters.

Influence of temperature

Sea surface temperature (SST) appears to have a strong influence over methyl bromide saturation. Groszko & Moore (1998) found a complex but robust correlation, with the ocean acting as a sink at high (>24 °C) and low temperatures (<12 °C), and as a source at intermediate temperatures. On this basis, an overall global sink of -10 Gg yr^{-1} was suggested (Groszko & Moore 1998). King *et al.* (2000) found a seasonal cycle in temperate open oceans (discussed above) and a relationship with SST. The relationship with SST accounted for 40-70% of the observed methyl bromide variability.

King *et al.* (2002) expanded the relationship with SST. Seven years of data (Lobert *et al.* 1995, 1996, 1997; Groszko & Moore 1998 and others) were used to generate a set of seasonally dependent quadratic equations (Equation 1.12 a-d).

Spring/Summer

$$\Delta\% = 0.17065\,t^2 + 1.91413\,t - 33.85196 \quad (t < 16\ °C) \qquad (1.12a)$$

$$\Delta\% = 0.48994\,t^2 - 26.70125\,t - 349.14043 \quad (t \geq 16\ °C) \qquad (1.12b)$$

Autumn/Winter

$$\Delta\% = 0.12519\,t^2 + 0.65604\,t - 40.00438 \quad (t < 16\ °C) \qquad (1.12c)$$

$$\Delta\% = 0.51728\, t^2 - 24.64675\, t - 262.91316 \quad (t \geq 16\ ^\circ C) \qquad (1.12d)$$

t = sea surface temperature (°C)

It was noted that this relationship between methyl bromide and SST is uncertain in some areas such as near-equatorial upwelling. The authors also postulated that the addition of another physical parameter linked to the precursors driving methyl bromide production and degradation (e.g. surface solar irradiance, mixed layer depth) would be necessary to predict methyl bromide fluxes more accurately.

Methyl bromide is supersaturated in surface seawater off NW Tasmania, with no evidence of any clear seasonal cycle (Sturrock *et al.* 2003). The observed super-saturations are in broad agreement with the relationships with SST derived by Groszko & Moore (1998) and King *et al.* (2000) in the 12-20 °C division, but not the seasonal equations of King *et al.* (2002).

Estimates of the global flux are sensitive to assumptions about the effect of temperature on production and destruction processes. For example, an early estimate of a net global methyl bromide sink (Lobert *et al.* 1995) was revised to a net source when accounting for regional and seasonal change to temperature (Pilinis *et al.* 1996). It is also important to consider the relative strength of biological degradation as well as physical removal processes. Chemical processes are largely responsible for the oceanic loss of methyl bromide in warmer waters of the Pacific and Caribbean, but biological losses predominate in the colder waters of the North Pacific Ocean, often showing a daily cycle (Tokarczyk *et al.* 2001, Tokarczyk & Saltzman 2001). A similar pattern is found in the Southern Ocean with chemical losses in warmer waters but predominantly biological uptake in colder southern waters (Tokarczyk *et al.* 2003). Removal of methyl bromide in coastal seawater can be associated with particulate matter, and may involve bacteria (King & Saltzman 1997).

Correlations to biology

Correlations between methyl bromide seawater concentration or sea-air saturation and phytoplankton biomass are sometimes found in high biomass coastal waters and in blooms of a single species. For example, methyl bromide at a coastal site in the

North Sea was supersaturated during a bloom of *Phaeocystis* sp. (Baker *et al.* 1999). Correlations between methyl bromide concentration and biological variables have been found less often in open ocean waters. Biological production of methyl halides may not be proportional to total phytoplankton biomass measured as Chlorophyll *a* (Chl *a*) since only some phytoplankton taxa produce them. Also, there are processes of biological removal that affect the net concentration. When biological destruction processes are strong, a negative linear relationship can be found between Chlorophyll *a* and methyl bromide production rates, such as in Labrador Sea waters with Chlorophyll *a* above 0.7 mg L^{-1} (Moore & Webb 1996).

However, there are some instances where there are correlations between methyl bromide concentration and a specific photosynthetic pigment other than Chlorophyll *a*, that indicates the presence of particular group of phytoplankton. For example, methyl bromide was super-saturated over a large region of the northeast Atlantic Ocean with a positive correlation to the pigment hexanoyloxyfucoxanthin, which is indicative of Prymnesiophytes including *Phaeocystis* sp. (Baker *et al.* 1999). Methyl bromide was also positively correlated with dimethyl sulfoniopropionate (DMSP), the precursor to DMS, indicating a common source to the compounds (Baker *et al.* 1999).

Partial lifetime

Butler (1994) found that the size of the methyl bromide ocean sink could be obtained by parameterisation of the air-sea exchange rate, and from measurements of the solubility, diffusivity and oceanic destruction rate of methyl bromide. Using the only known chemical loss rates for methyl bromide in the ocean, Jeffers & Wolfe (1996) calculated a partial lifetime of 3.7 years. Refinements including better spatial resolution and inclusion of biological destruction in the ocean led to a calculation of gross oceanic uptake of 77 Gg and partial lifetime of 1.8 to 1.9 years (Yvon & Butler 1996, Yvon-Lewis & Butler 1997). Coupling this with the 16 Gg yr^{-1} net flux estimate (from King *et al.* (2000) above) results in an estimate of 61 Gg yr^{-1} gross source.

1.5.3 Ocean source of methyl iodide

Specific areas of ocean can act as a net source and a sink of methyl iodide depending on saturation, but overall the ocean is a net source to the atmosphere. Specific estimates of the fluxes from the oceanic sources to the atmosphere vary widely, from 40,000 Gg yr^{-1} (Lovelock *et al.* 1973), 1,300 Gg yr^{-1} (Rasmussen *et al.* 1982b), 400 Gg yr^{-1} (Singh *et al.* 1983), 800 Gg yr^{-1} (Reifenhäuser & Heumann 1992) and ~250 Gg yr^{-1} (Moore & Groszko 1999). The more recent estimates tend towards the lower end of the range. Methyl iodide has a short lifetime of a few days, so the atmospheric concentration is low but the fluxes from the ocean to the atmosphere are large, of the order of hundreds of Gg yr^{-1} (Carpenter *et al.* 1999). Other iodinated species (including CH_2I_2 etc.) are even shorter lived and this effect of low concentration but high flux is further exaggerated. So methyl iodide may represent a lower proportion of the total iodine atom flux to the atmosphere than the concentration suggests (Carpenter *et al.* 1999). The proportion of iodine present as methyl iodide compared to other species varies in different regions.

Since the earliest measurements of methyl iodide were taken it has been thought that the major oceanic source was production by marine organisms (e.g. Lovelock 1975, Lovelock *et al.* 1973, Moore *et al.* 1993, Rasmussen *et al.* 1982b). Production by macroalgae and phytoplankton was identified and measured in field and laboratory studies (Chameides & Davis 1980, Klick & Abrahamsson 1992, Oram & Penkett 1994, Rasmussen *et al.* 1982b) but there has been some question whether these sources are significant compared to the total global source (Yokouchi *et al.* 2001). Macroalgal biomass is restricted to coastal waters, and represents a corresponding low source, 0.01 to 0.1 Gg yr^{-1} (Giese *et al.* 1999, Manley *et al.* 1992, Nightingale *et al.* 1995). Phytoplankton are widely distributed throughout all oceans and have a much greater global biomass than macroalgae. Phytoplankton have been shown to produce methyl iodide, but the measured production rates of 1-10 Gg yr^{-1} may be insufficient to account for the global flux to the atmosphere (Itoh *et al.* 1997, Manley & de la Cuesta 1997).

Other processes have been proposed as the major marine source of methyl iodide to the atmosphere, including the photochemical production of methyl iodide in seawater (Moore & Zafiriou 1994, Happell & Wallace 1996, Yokouchi *et al.* 2001, Richter

2003). Amachi *et al.* (2001) showed that some terrestrial and marine bacteria methylate environmental levels of iodide (0.1 μM) to produce methyl iodide, suggesting bacteria could be the major source. Presently, there is no rigorous quantification of the input from different sources and any source could be incorrectly estimated. However it seems likely there is input from multiple sources in the marine system, including a source from marine biota.

Methyl iodide saturation by region

Methyl iodide is substantially super-saturated in large areas of the world's oceans, including the waters of the northwest Atlantic, northeast Atlantic and the Pacific Ocean (Moore & Groszko 1999). Large sub-surface maxima in methyl iodide concentrations have been observed in many oceans (Moore & Groszko 1999, Smythe-Wright *et al.* 2006).

Measurements along transects through the Pacific Ocean, showed concentrations of 2 to 7 pM and a clear latitudinal trend (Moore & Grozsko 1999, Figure 1.7a). A similar pattern was found in methyl iodide concentration in air above the sea along transects in the western Pacific Ocean (0.5 to 5.0 pptv) and South East Asian seas (0.24 to 2.0 pptv), with higher concentrations at mid-latitudes than the equator (Yokouchi *et al.* 1997). Measurements along extensive transects from the northeast Atlantic Ocean down to the Southern Ocean and Antarctica (50°N to 60°S) showed a different pattern, with seawater concentration of methyl iodide ranging from 0.25 to 18.68 pM (mean 4.37 pM) with a strong relationship to sea surface temperature and high concentrations measured in frontal regions (Chuck *et al.* 2005, Figure 1.7b).

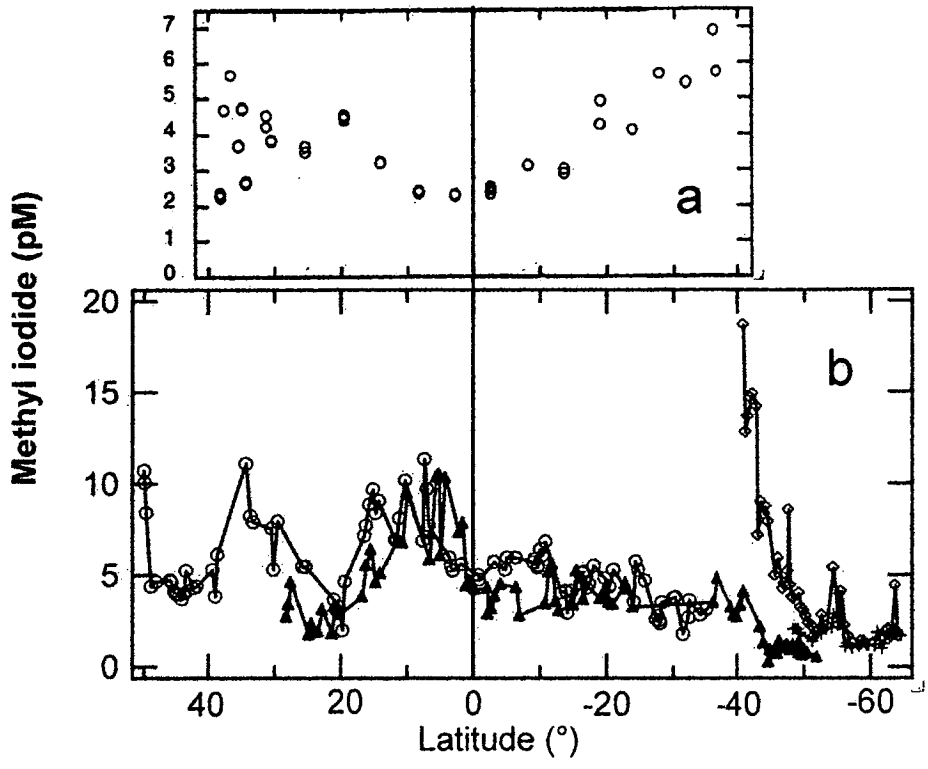

Figure 1.7 Methyl iodide concentration in seawater of the open ocean measured in (a) Pacific Ocean transect (source: Moore & Groszko 1999) and (b) three Atlantic Ocean cruises (source Chuck *et al.* 2005)

However, these measurements were only of surface samples. The peak in methyl iodide concentration can be below the surface. Pronounced sub-surface maxima of methyl iodide were measured in the Sargasso Sea and Pacific Ocean, but not in the Labrador Sea (Moore & Groszko 1999). Sub-surface maxima can also be present for CH_2I_2 (Moore & Tokarczyk 1993, Yamamoto *et al.* 2001). A large dataset of methyl iodide measurements to 150 m depth have been made over a large geographic area in the Atlantic, Pacific and Indian Oceans (Smythe-Wright *et al.* 2005; Smythe-Wright *et al.* 2006). Seawater concentration of methyl iodide ranged from below the detection limit up to 45 pM, with highest values in the lower latitudes, and always with a sub-surface maxima. A transect through the Atlantic Ocean from Iceland to west Africa is shown in Figure 1.8, showing a clear latitudinal pattern. Strong correlations between seawater concentration of methyl iodide and biomass of the *Prochlorococcus* group of picoplankton, together with emission measured in laboratory studies on this species, suggest there is a large source from this plankton alone.

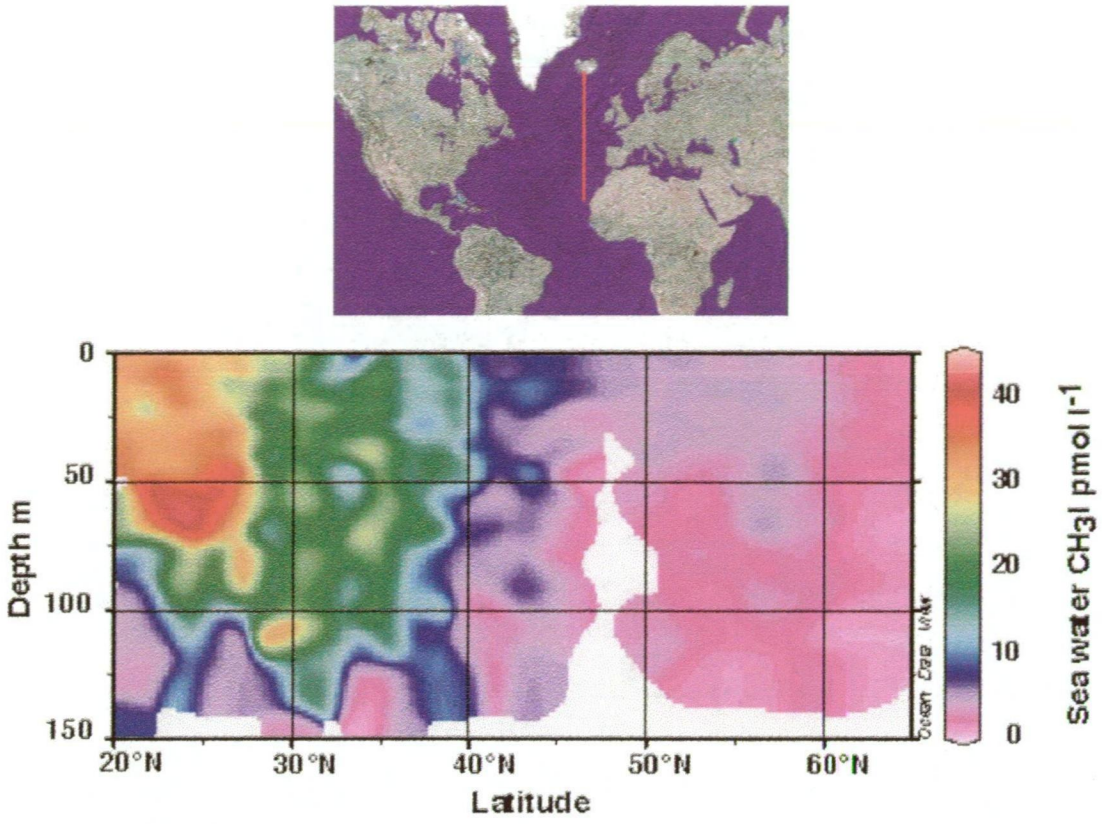

Figure 1.8 Depth profile of methyl iodide concentration in seawater along a transect in the north Atlantic Ocean, cruise track is shown as a red line in small map (source Smythe-Wright *et al.* 2006)

1.5.4 Coastal and inshore waters

There is generally a decrease in methyl halide concentration in seawater moving away from the coast. For example, methyl iodide is generally higher in inshore waters and decreases offshore (Moore & Tokarczyk 1993, Baker *et al.* 2000). This pattern of decrease can extend from coastal waters out to the open ocean. At Mace Head in Ireland, methyl iodide in seawater decreases from a high concentration at the coast (15.07 ± 4.15 pM at 100 m) to lower concentrations in coastal waters (9.72 ± 1.9 pM at 2-10 km), decreasing again in shelf waters (2.8 to 4.2 pM at 30 km), and lower still off the shelf (0.7 to 1.7 pM) (Carpenter *et al.* 2000, Baker *et al.* 2000). The latter measurements are from a field campaign in 1997 and are displayed in Figure 1.9 (source Baker *et al.* 2000). The range shown here is similar to measurements taken in the same area during 1996 (mean 3.4 pM, range 1.2-8.2 pM, Moore & Groszko 1999). There has been considerable work done in the Cape Grim region on coastal waters, which forms the basis for this thesis (Sturrock *et al.* 2003, Corno 2001, Corno *et al.* 2004), more details are given in Chaper 4.

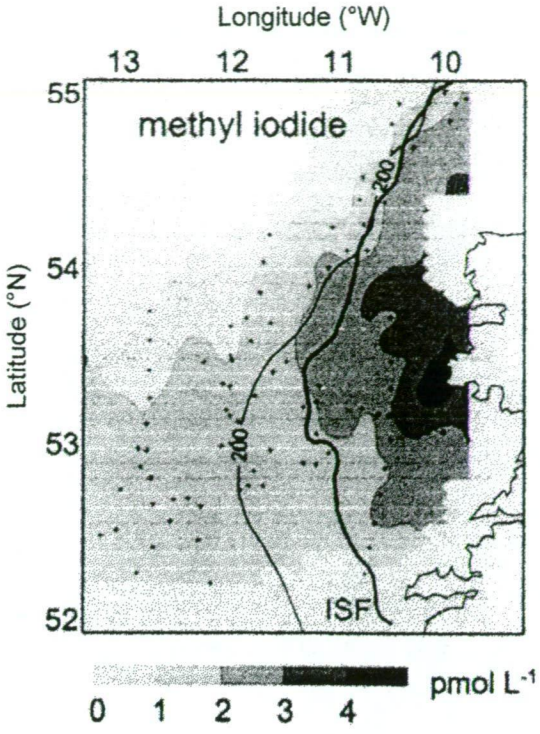

Figure 1.9 Methyl iodide concentration in seawater measured in coastal waters and open ocean off the west coast of Mace Head, Ireland in May 1997 (source: Baker *et al.* 2000)

Coastal waters can have a higher and more variable concentration of methyl halides than the open ocean. There is temporal variability on a number of scales: daily, weekly, monthly, seasonal, inter-annual. There are few time series of methyl halides in coastal waters that allow an analysis of seasonal changes. Baker *et al.* (1999) measured phytoplankton and methyl bromide concentrations over an entire season at two sites in the coastal waters of Norfolk, eastern England (Site 1 was 4 miles offshore in 30 m depth and site 2 miles offshore in 7 m depth). Methyl bromide concentration was 2 to 3 pM from February to June, with saturations of 40 to 80%, followed by a peak of 300% supersaturation in June (8.7 pM in seawater) concurrent with a bloom of *Phaeocystis* sp., followed by another smaller peak in August and then a steady decline and under-saturation from late September until February. Overall, methyl bromide was supersaturated for three months of summer, with the greatest super-saturation during the bloom of *Phaeocystis* sp. (Baker *et al.* 1999).

Archer *et al.* (2007) found a repeating seasonal cycle of methyl iodide concentration in coastal waters in the English Channel, with a range of more than an order of

magnitude (6 to 146 pM, mean 61 pM). The maximum was in summer to autumn and the minimum was in winter, and this cycle is also present in sea-to-air fluxes. Methyl iodide concentration was correlated closely with C_2H_5I, CH_2ClI and CH_2I_2 concentrations.

Seasonal cycles are present in the atmospheric records of many halogenated compounds at air monitoring stations. Monthly shipboard measurements of methyl iodide concentration in air over the open northwest Pacific Ocean also showed a sinusoidal seasonal cycle with more than a 20-fold concentration range (0.08 to 1.95 pptv, Yokouchi *et al.* 2001). These seasonal cycles are related to seasonal cycles in the relevant source and sink terms, including strong sources from coastal waters. For example, the seasonal cycle of methyl iodide with a summer maximum and winter minimum measured at a ground station in eastern England (Oram & Penkett 1994) correlates well with the seasonal cycle found in the English Channel (Archer *et al.* 2007).

Methyl iodide concentrations in New Zealand coastal waters were measured to be between 2 to 6 pM, similar to the general trend of concentration across the open Pacific Ocean, but this cruise track did not go close to shore (Moore & Groszko 1999).

1.5.5 Forms and conversions of iodine in the ocean

Iodine exists in dissolved and particulate forms in oxic seawater (Wong 1991), the major forms being iodate (IO_3-) and iodide (I-). Iodate predominates in deep waters (Tsugonai 1971), but in surface waters there is a greater proportion of iodide. The major chemical reaction in these surface waters is the inter-conversion between iodate and iodide through chemical reduction (Truesdale *et al.* 2000). This reduction has been linked to phytoplankton growth and microbial activity (Wong & Hung 2001; Truesdale & Bailey 2002, Truesdale *et al.* 2000, Campos *et al.* 1996), but there may be a role of photochemistry (Spokes & Liss 1996) and sediment-water interaction. The link to phytoplankton was deduced from the seasonality in the cycle, and correlations with nutrient concentrations and cycling. In an open ocean upwelling zone, decrease in iodate concentration was matched closely by an increase in iodide concentration, and this change was strongly correlated with nitrate

reductase activity (nitrogen metabolism by cells) (Wong & Hung 2001). However, this is not present in all situations. For example, experiments conducted in a relatively large enclosed chamber that simulates real-life conditions, but allows the manipulation of environmental factors (a 'mesocosm') show that integrated iodate and total iodine concentrations do not vary significantly under simulated phytoplankton bloom conditions (Truesdale *et al.* 2003). Methyl bromide and methyl iodide were monitored during the Southern Ocean iron enrichment experiment (SOFeX) north of the Antarctic Polar Front (Wingenter *et al.* 2004). The seawater concentration of methyl bromide increased inside the fertilized patch (6.5 ± 0.1 pptv inside, 5.7 ± 0.1 pptv outside) and was correlated weakly with productivity, which suggests an increase in methyl bromide production and a decoupling of the production and removal processes. In contrast, methyl iodide was observed to decrease in the fertilized patch (4.94 ± 0.07 pptv inside, 6.4 ± 0.2 outside) negatively correlated with CO_2 uptake and O_2, suggesting increased microbial oxidation.

Iodide concentration in relation to methyl iodide and other low molecular weight organo-iodine compounds may be expected to follow one of two relationships. Production of each may be competitive, in which case the concentrations would be inversely related. Alternatively the production of each may be linked or synergistic, where the concentrations of each would be positively correlated. The conversion of iodate to iodide can be related to biological processes and these processes are thought to be associated with the haloperoxidase enzyme at the cell surface (Küpper *et al.* 1998). These processes are not associated with the blooming or logarithmic growth of phytoplankton, but are generally associated with macronutrient depletion and conditions where dissimilatory processes outweigh assimilatory processes in the stationary phase or into senescence (Butler *et al.* 2007). This means that the biological source of both iodide and reduced forms of iodine (including methyl iodide) may be both generally related to total biomass of phytoplankton but at different stages of growth. Biological conversion between different forms of iodine associated with marine phytoplankton and bacteria is summarized in Figure 1.10. Further details are found in Butler *et al.* (2007) in Appendix 1.

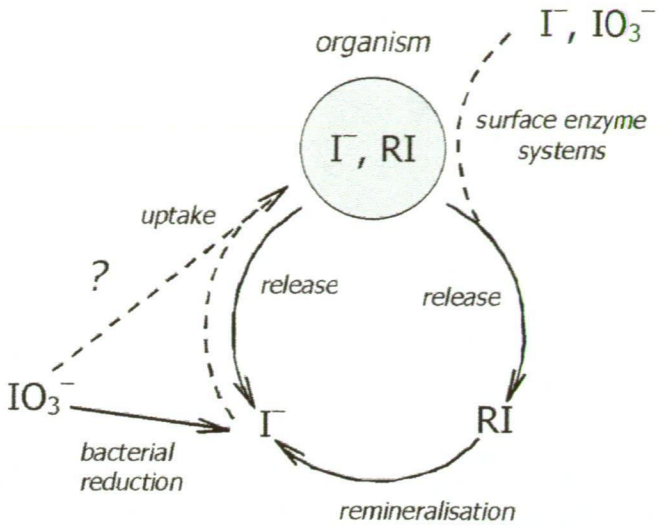

Figure 1.10 Interconversion of iodine species associated with the uptake and release at the cell surface (RI denotes a reduced form of iodine including methyl iodide, blue circle represents a single-cell marine organism, dashed lines represent multi-step processes), meta-stable intermediates (e.g. I_2, HIO) are not shown (Source Butler *et al.* 2007)

1.6 Macroalgae

Macroalgae are a source of halocarbons, including methyl bromide and methyl iodide. The source from macroalgae varies according to species, and also to conditions. Ultraviolet light can stimulate the emission of halocarbons from submerged macroalgae (Laturnus *et al.* 2004). Exposure to the air that induces photo-oxidative stress can initiate emission of methyl halides, polyhalogenated compounds and I_2 (Collen *et al.* 1994, Laturnus *et al.* 2004, Palmer *et al.* 2005). This can result in a pattern of inshore halocarbon concentration correlated with tidal cycle (Carpenter *et al.* 1999). A pulse of emission of methyl iodide from *Ascophyllum nodosum* occurs when it is re-immersed in seawater after a period of drying, simulating the effect of tide (Nightingale *et al.* 1995). In addition, production of methyl iodide by bacteria associated with rotting kelp has been suggested to be globally significant, for example the bacterial emission associated with giant kelp may be greater than emission from the kelp itself (Manley & Dastoor 1988).

1.6.1 The source from macroalgae in context

The intensity and global significance of biogenic coastal emissions of methyl halides can be given context by comparing them to those from the open ocean. Macroalgae

can be present in very high density but are restricted to the shoreline, phytoplankton has a lower density, but is present throughout the world's oceans. Open ocean covers ~70% of the earth's surface whereas coastal areas covers only ~0.3% (Baker *et al.* 2001).

These differences in both density and in aerial extent of macroalgae and phytoplankton are reflected in the flux rates and global source of the methyl halides. Methyl iodide is produced and emitted in the open ocean at rates of 15 nmol m^{-2} d^{-1} in the Southern Ocean (Chuck *et al.* 2005) and 23 nmol m^{-2} d^{-1} in the Atlantic Ocean (Richter & Wallace 2004), and represents a global source of 1 to 2 Tg yr^{-1}, or approximately 3 to 7% of the total global flux (Davis *et al.* 1996). Fluxes of methyl iodide from seaweeds at the coast have been measured at 100 nmol m^{-2} d^{-1} (Zhou *et al.* 2005), but the total global source is only 2.8 Gg yr^{-1}, which is < 0.1% of the global source (Baker *et al.* 2001). Similarly, flux rates of methyl bromide from macroalgae can be high, but the global source is only ~0.06 Gg yr^{-1} which is also < 0.1% of the total global source (Baker *et al.* 2001).

It is still unclear what the dominant pathway of methyl halide production in the open ocean is, whether from biological origin (Smythe-Wright *et al.* 2006, Chuck *et al.* 2005) or from abiotic photochemistry (Moore & Zafiriou 1994, Richter & Wallace 2004, Yokouchi *et al.* 2001). The production and emission of methyl halides at the inshore environment can be more easily linked to biological activity of macroalgae. Different species of macroalgae emit different suites of halogenated gases, and in varying quantities. The emission of halogenated gases from coastal macroalgae beds has been measured in various locations in various ways. Production by macroalgae has been deduced through measurements made at air monitoring stations (discussed in Chapter 2), through enrichments in macroalgal beds and through laboratory studies.

1.6.2 Enrichments

Elevations, or 'enrichments' of halocarbon concentration, have been measured associated with seaweed beds. These enrichments of methyl halide concentration can be in the air directly above seaweed beds compared to background concentrations in air, in rock pools compared to coastal seawater, and in coastal seawater compared to

water outside beds. Enrichment is often calculated as an enrichment factor, or ratio. Enrichment of halogenated gases was first reported in air above beds of the brown kelp Oarweed (*Laminaria digitata*) by Lovelock *et al.* (1973), and then in seawater among beds (Lovelock 1975), showing an enrichment of 1000 times for methyl iodide compared to open Atlantic Ocean seawater. Enrichment of halogenated gases was then reported associated with other species of seaweeds (Fenical 1975, 1981; Hewson & Hager 1980, Gschwend *et al.* 1985).

Enrichment of $CHBr_3$, CH_2Br_2 and $CHBr_2Cl$ was found within *Fucus* beds in Sweden, but not of CH_2I_2 or CH_2ClI (Klick 1992). In a separate study, air above a *Fucus* bed was found to have a strong enrichment of methyl iodide (8.5 times) as well as methyl bromide and methyl chloride, compared to background concentrations at Mace Head station (Bassford *et al.* 1999). At a coastal site in the east of England, enhancements of 1.5 to 2.5 for methyl iodide and 1.0 to 1.2 for methyl bromide were measured above beds of various macroalgae including *Fucus*, compared to air on an adjacent cliff top (Baker *et al.* 2001). Enhancement factors of 4.3 for methyl iodide and 1.4 for methyl bromide were found in rock pools at this same location (Baker *et al.* 2001). A similar enhancement of methyl iodide (approximately 3.9) was found in rock pools by Nightingale *et al.* (1995), along with enhancement of 1.76 for methyl iodide in seawater near beds of *Laminaria digitata* compared to waters offshore. Enrichment of methyl iodide near beds of *Laminaria* and *Fucus* kelps at the Mace Head station in Ireland has been shown to be very high. Enrichment of methyl chloride, methyl bromide and methyl iodide were also found in beds of *Macrocystis pyrifera* (Manley & Dastoor 1987).

1.6.3 Laboratory studies

Laboratory incubations have shown production of methyl halides by green, brown and red algae (Gschwend *et al.* 1985, Laturnus *et al.* 1998a, 1998b, Schall *et al.* 1994), but emission is eight times higher in the kelps compared to non-kelps (Manley *et al.* 1992). These studies have used fresh or dried kelp pieces placed in a chamber, measured as fresh weight (FW) and dry weight (DW). Various species examined by Baker *et al.* (2001) showed production of methyl bromide in the range 0.004 to 1.49 ng g DW^{-1} h^{-1} and methyl iodide in the range -1.2 to 2.7 ng g DW^{-1} h^{-1}. A number of

species measured by Nightingale *et al.* (1995) produced methyl iodide in the range 0.004 to 1.25 ng g $DW^{-1}h^{-1}$. *Laminaria* kelps produce up to 2.6 ng g $FW^{-1}h^{-1}$ (Manley & Dastoor 1988), and 0.875 ng g $DW^{-1}h^{-1}$ (Nightingale *et al.* 1995). *Laminaria digitata* kelp has also been shown to emit CH_2I_2 in laboratory experiments (Palmer *et al.* 2005). Emission of 0.6 ng g $FW^{-1}h^{-1}$ of methyl iodide and 0.2 ng g $FW^{-1}h^{-1}$ of methyl bromide was measured from *Macrocystis pyrifera* (Manley & Dastoor 1987). Through laboratory studies it was found that the emission of halocarbons by macroalgae can be affected by abiotic factors such as light, salinity, nutrient availability (Laturnus *et al.* 2000), and UV light (Laturnus *et al.* 2004).

1.7 Phytoplankton

Biological production of methyl halides by phytoplankton has been suspected since the earliest measurements of methyl halides in the ocean. The significant production of methyl halides by macroalgae suggested that microalgae may possess similar processes. Also, concentrations of methyl halides can be significantly above saturation in areas of open ocean surface waters (e.g. Singh *et al.* 1983), and these can occasionally be correlated with phytoplankton distributions (Klick 1992, Klick & Abrahamsson 1992, Moore & Tokarczyk 1993), suggesting that a production mechanism can be associated with phytoplankton. Ascertaining the exact nature of the source of methyl halides from field measurements can be problematic, in particular distinguishing between phytoplankton and bacterial production (Moore *et al.* 1994). This has led to several laboratory studies of phytoplankton in isolation. These are outlined below and summarized in Table 1.3.

Table 1.3 Phytoplankton culture species and the measured production of halogenated compounds

Group	Species	CH_3Br	CH_3I	CH_3Cl	$CHBr_3$
Diatom	*Odontella mobiliensis*			✓[3]	x[2]
	Phaeodactylum tricornutum	✓[5,5,7]	✓[5,5]	✓[3,5,5,7]	
	Thalassiosira weissflogii	✓[5,5]	✓[5,5]	✓[3,5,5]	
	Porosira glacialis	✓[8]	✓[8] Σ[5]	✓[3]	✓[2]
	Nitzschia seriata	x[8]	x[8]	✓[3]	x[2]
	Nitzschia sp. CCMP 580	✓[8]	✓[8]	✓[3]	
	Nitzschia sp.		✓[5]		✓[2]
	Nitzschia punctata		£[5]		
	Nitzschia pungens	✓[8]	x[8]		x[2]
	Nitzschia arctica				
	Skeletonema costatum		x[5]		
	Chaetoceros neogracile		x[5]		
	Chaetoceros diversum	✓[6]			
	Chaetoceros atlanticus	✓[6]			
	Chaetoceros sp.	x[6]			x[2]
	Chaetoceros calcitrans	✓[7]		✓[7]	
	Navicula sp.	x[8]	x[8] ✓[5]		x[2]
	Synedra miniscula	x[6]			
	Thalassiosira pseudonana	x[6]	✓[5]		
	Thalassiosira gravida				x[2]
Chlorophyte	*Pycnococcus provasolii*		x[5]		
	Dunaliella parva		x[5]		
Chrysophyte	*Coccolithus pelagicus*		x[5]		
	Emiliania huxleyi	✓[7]	x[5]	✓[7]	
	Isochrysis galbana		x[5]	✓[3]	x[2]
Cryptophyte	*Guillardia theta*	✓[6]			
	Hemiselmis rufescens	✓[6]			
Cyanobacteria	*Synechococcus sp.*	✓[7]	x[5]	✓[7]	
	Synechococcus bacillaris	x[6]			
Dinoflagellate	*Gymnodinium sp.*		x[5]		
	Amphidinium carterae	✓[6]			
	Crypthecodinium cohnii	✓[6]			
	Prorocentrum micans	✓[6]			
	Prorocentrum sp.	✓[7]		✓[7]	
Haptophyte	*Isochrysis sp.*	x[7]		✓[7]	
Prasinophyte	*Pycnococcus provasolii*	✓[6]			
	Tetraselmis levis	x[6]			
	Tetraselmis sp.	x[7]		✓[7]	
Prymnesiophyte	*Emiliania huxleyi*	x[6]		✓[7]	
	Pavlova sp.	✓[6]			
	Pavlova gyrans	✓[6]			
	Pavlova lutheri	✓[6]			
	Phaeocystis sp.	✓[6,7]	✓[5,5]	✓[7]	
	Pleurochrysis carterae	✓[6]			
Rhodophyte	*Porphyridium sp.*	✓[7]		✓[7]	
Prochlorococcus			✓[9]		
Arctic Ice Algae					✓[1]
Antarctic Ice Algae					✓[1]

blue = non-axenic £ = Negative production Σ = +ve during log growth, -ve during stationary growth

1. Sturges *et al.* (1992), 2. Tokarczyk & Moore (1994) 3. Tait & Moore (1995)
4. Scarratt & Moore (1996) 5. Manley & de la Cuesta (1997) 6. Saemundsdottir & Matrai (1998)
7. Scarratt & Moore (1998) 8. Moore *et al.* (1996) 9. Smythe-Wright *et al.* (2006)

1.7.1 Phytoplankton studies

Laboratory measurements of methyl halide production by phytoplankton were initially made in the early to mid nineties by the research group led by Dr Robert Moore of Dalhousie University. Numerous other studies have been performed since.

Moore & Tokarczyk (1993) detected methyl iodide production by one species of phytoplankton. Tokarczyk & Moore (1994) detected the production of volatile organohalogens ($CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$, and CH_3CII) in the cold-water diatoms *Porosira glacialis* and *Nitzschia* sp. Tait & Moore (1995) detected the production of methyl chloride by seven species of warm and cold-water phytoplankton. Scarratt & Moore (1996) measured the production of methyl chloride, methyl bromide and methyl iodide in two axenic cultures (*Phaeodactylum tricornutum, Thalassiosira weissflogii*) and one non-axenic culture (*Phaeocystis* sp.) of marine phytoplankton under various nutrient regimes. There were no consistent differences in production between different nutrient regimens or between axenic and non-axenic cultures and methyl halide production was not directly dependent on photosynthesis. *Phaeocystis* sp. had the highest production rate, *T. weissflogii* the lowest.

Scarratt & Moore (1998) quantitatively measured methyl bromide and methyl chloride production and non-quantitatively observed methyl iodide production from nine species of phytoplankton (see Table 1.3). All but two were grown in axenic conditions, and axenic and non-axenic controls were also tested. Manley & de la Cuesta (1997) measured methyl iodide production by fifteen species of marine phytoplankton and five species showed significant increases in methyl iodide.

Moore *et al.* (1996) examined the production of polyhalogenated compounds ($CHBr_3$, CH_2Br_2, CH_2I_2) by the diatoms *Nitzschia* sp., *Nitzschia arctica* and *Porosira glacialis* by bromoperoxidase and iodoperoxidase enzymes. Methyl chloride and methyl bromide were produced in significant levels in these same three cultures, and also some other species (see Table 1.3). It was concluded that the production of the methyl halides occurs by different mechanisms from those for polyhalogenated compounds and independent of haloperoxidases. Methyl iodide was produced in *Nitzschia* sp. and in *Porosira glacialis* only under high light, and was shown to be by an independent mechanism to other compounds.

Saemundsdottir & Matrai (1998) studied the production of methyl bromide in coastal and open ocean marine phytoplankton cultures, with 13 of the 19 species tested produced methyl bromide in the range 1.7 to 30.1 pg CH_3Br μg^{-1} Chl *a* d^{-1}. The highest producer was *Phaeocystis* sp. Coastal species appeared to be stronger producers of methyl bromide than open ocean species. Cold water (4 °C), temperate (15 °C) and tropical (22 °C) species all displayed methyl bromide production, with no apparent trend due to temperature. Also, the heterotrophic dinoflagellate *Crypthecodinium cohnii* that is often found associated with decaying macroalgae produced significant amounts of methyl bromide.

Baker *et al.* (1999) didn't perform culture studies, but examined field measurements of methyl bromide and the prymnesiophyte *Phaeocystis* sp. A pigment characteristic of *Phaeocystis* sp. (hexanoyloxyfuocoxanthin) was correlated with seawater methyl bromide concentration, indicating a source from this species. High values of methyl bromide were observed during the senescence of *Phaeocystis* sp. Smythe-Wright *et al.* (2006) confirmed field measurements of production of methyl iodide by *Prochlorococcus* sp. in laboratory studies.

1.7.2 Sea ice studies

Sturges *et al.* (1991) measured bromoform production rates by arctic ice algae in controlled experiments. Sturges *et al.* (1992) measured $CHBr_3$ emission in laboratory incubations of microalgae from beneath arctic annual ice and found that they could be a larger global source of bromoform than macrophytes. Following this, Sturges *et al.* (1993) measured the release of CH_2Br_2, $CHBr_2Cl_2$ and $CHBrCl_2$ in laboratory incubations of ice-algae from the Antarctic. There was evidence that methyl bromide also increased in the incubations. Also, methyl bromide concentrations in ambient air directly above different regions were measured, and were highest over sea ice and the ice edge. However, the measurements taken during a bloom of *Phaeocystis* sp. phytoplankton and above a surface infiltration pond containing microalgae were not significantly elevated above other samples from the same regions.

Moore *et al.* (1993) found elevated levels of bromoform and dibromomethane in arctic ice cores, but distinguishing between the effect of phytoplankton, zooplankton,

bacteria and macrophytes was not possible. Moore *et al.* (1994) detected the release of volatile organohalogens ($CHBr_3$, CH_2Br_2, CH_2ClI, and $CHBr_2Cl$) in *in situ* bottle incubations of ice-algae from the Arctic. Following this, uni-algal cultures were found to release this same suite of organohalogens, but the effect of bacteria could not be distinguished. Methyl chloride release was observed, but was surmised to be due to the involvement of bacteria. Fogelqvist & Tanhua (1994) found significantly elevated concentrations of methyl iodide in ice pore water in Antarctic sea ice algae bottom communities, along with other iodated species.

1.7.3 Stage of growth

Numerous studies have measured higher rates of methyl halide production in the stationary stage of growth or in senescence compared to log-phase growth (Tokarczyk & Moore 1994, Tait & Moore 1995, Scarratt & Moore 1998, Saemundsdottir & Matrai 1998, Smythe-Wright *et al.* 2006), or even after cell death (Tait & Moore 1995). Tait & Moore (1995) concluded that because methyl chloride production increased after the death of all cells, there was a combination of production pathways, not just from active metabolism in growing cells. The production mechanism of all three methyl halides during senescence were found by Scarratt & Moore (1998) to reside within intact cells, not in exuded material and production was not observed when cells were lysed.

Methyl bromide production has been reported to increase rapidly in the stationary and senescent phases of growth in the cultures tested (Saemundsdottir & Matrai 1998). The authors hypothesized this to be due to (a) methyl bromide being produced and stored during growth but only released as the cells age and die, or (b) as algal cells age, production and release of methyl bromide increases, bacteria colonise the cells and aid in the production or release of methyl bromide, or a combination of both of these.

However, other studies have found that some species show positive production of methyl iodide during log growth but negative production during stationary growth, such as for the diatom *Porosira glacialis* (Manley & de la Cuestra 1997).

1.8 Methyl halide production processes

To understand the ocean-atmosphere cycles of methyl halides, including the spatial and temporal variability of the marine source, an understanding of the details and function of the processes is helpful. There are photochemical and biological processes of methyl halide production in surface oceans. Some specific aspects of these processes are outlined below.

1.8.1 Photochemical production

Photochemical production of methyl iodide occurs in seawater that has been filtered of all biology when exposed to sunlight (Moore & Zafiriou 1994). This formation of methyl iodide from photochemically produced methyl and iodide radicals is a potentially significant source of methyl iodide in surface ocean waters to the atmosphere (Moore & Zafiriou 1994, Yokouchi *et al.* 2001, Richter 2003). Happell & Wallace (1996) found no correlation between methyl iodide saturation and biology and the only significant correlation with a physical variable was with photosynthetically active radiation (PAR). This finding was also supported by deck incubation experiments, which showed a strong effect of light and little effect of biological activity in oligotrophic tropical waters (Richter & Wallace 2004). The process is inhibited by oxygen and enhanced by high iodide concentration. Production is higher in coastal waters due to the higher concentration of organic material acting as a light absorber and a methyl radical source (Moore & Zafiriou 1994). Photochemical production of methyl bromide and methyl iodide also occurs in surface snow in Greenland (Swanson *et al.* 2002).

1.8.2 Biological production

Marine macroalgae and phytoplankton produce a greater diversity of brominated, iodinated and chlorinated compounds than terrestrial organisms, perhaps reflecting the non-depleting source of seawater halogens (Neidleman & Geigert 1986; Gribble 1992). The biochemical pathway involved in the biological production of methyl halides is distinct from that of the production of polyhalomethanes. Biological production of methyl halides occurs via methyltransferase activity whereas

polyhalomethanes are a byproduct of halogenation of certain organic molecules by haloperoxidases (Theiler *et al.* 1978, Wuosmaa & Hager 1990). Cyanobacteria, algae, higher plants and fungi all produce methyl halides by the same mechanism: the enzymatic methylation of halogen ions (Cl^-, Br^- or I^-) by methyl transferases (White 1982; Wuosmaa & Hager 1990; Ni & Hager 1999). There appears to be at least two different methyl halide transferases; one type is found only in the family *Brassicaceae* (Attieh *et al.* 1995) and the other type methylates only halides and is found in fungi and algae. This second type of enzyme involves the enzymatic synthesis of methyl halides through an *S*-adensoyl methionine (SAM) transfer mechanism, and was first detected in cell extracts of a marine red alga (Wuosmaa & Hager 1990). An additional survey of marine algae showed that 22 out of 44 algae collected were methyl chloride producers and the methyl transferase reaction was thought to be the mechanism in all these algae (Wuosmaa & Hager 1990). The production of polyhalogenated compounds ($CHBr_3$, CH_2Br_2, CH_2I_2) by laboratory cultures of the diatoms *Nitzschia* sp., *Nitzschia arctica* and *Porosira glacialis* was proposed to be via bromoperoxidase and iodoperoxidase enzymes (Moore *et al.* 1996).

The Michaelis-Menten constant (K_M) of an enzyme is the substrate concentration that allows the reaction to proceed at one-half its maximum rate, a low K_M means the enzyme reaches its maximum catalytic rate at a low concentration and the enzyme binds to its substrate very tightly. The values of K_M for methyltransferases suggest that halides are not the intended substrate (methyl acceptor), since they are high compared to the K_M of SAM and there is not a high catalytic efficiency in the reactions (Manley 2002).

Marine bacteria can be a source of methyl halides (Amachi *et al.* 2001, 2004, Fuse *et al.* 2003) but can also remove methyl halides from the oceans (Oremland *et al.* 1994, King & Saltzman1997, Goodwin *et al.* 1998, Hoeft *et al.* 2000, Trotsenko *et al.* 2003), as well as in estuarine, freshwater and hypersaline conditions (Connell *et al.* 1997, Goodwin *et al.* 1998). The oxidization of methyl halides by marine bacteria is through a methyltransferase pathway (Schafer *et al.* 2005).

1.8.3 Function of methyl halide production

Halomethanes are secondary compounds in cell processes. Unlike primary compounds, they are not associated with basic metabolism, photosynthesis, respiration or common biosynthetic pathways (Manley 2002). The function of many of the compounds associated with secondary metabolism are not known or verified. Also, many secondary compounds may not have a function, the compound may be part of a 'metabolic experiment' whereby an evolutionary advantage does not yet exist. If plants are not limited by carbon or critical nutrients, they may have carbon available for experimentation. An example is the production of halogenated secondary antibiotics by terrestrial fungi to protect against bacterial attack (Manley 2002). These antibiotics would probably have been the product of 'experimentation' with the production of secondary compounds that then fulfilled a function, thereby conferring a competitive advantage. It is not yet clear whether the methylation of halides and the production of methyl halides perform a function in macroalgae and phytoplankton, nor if this has given them a selective advantage. Except for some fungi, an evolutionary advantage of producing halomethanes may not presently exist (Manley 2002).

Some inferences about the function of methyl halide production may be made from studies involving environmental variables and stresses. Macroalgal production of methyl iodide is influenced by stress from light intensity, desiccation, tissue wounding, herbivore grazing stresses (Nightingale *et al.* 1995) and added hydrogen peroxide (Pedersen *et al.* 1996). Photo-oxidative stress when seaweed is exposed to the air is known to initiate emission of methyl iodide, polyhalogenated compounds and I_2 (Collen *et al.* 1994, Palmer *et al.* 2005), often resulting in a pattern of inshore methyl iodide concentration correlated with tidal cycle (Carpenter *et al.* 1999). Therefore, methyl iodide production is not necessarily linked to photosynthetic pathways but may be linked to stress responses. By contrast, methyl iodide production by phytoplankton is not linked to light or light induced stress (Hughes *et al.* 2006) so is probably not linked biochemically to the photosystem reactions in the cell, nor to light stress reactions. Six possible functions for methyl halide production have been proposed in the literature, discussed below.

As a methyl donor

In many white rot fungi, methyl chloride is a methyl donor in the biosynthesis of the secondary compounds and emission of methyl chloride occurs when there is an uncoupling of the biosynthetic and utilizing mechanisms in the membrane (Harper 2000). This is associated with the wood rotting mechanism of these fungi and is therefore not present in other organisms, including phytoplankton. There may be other undiscovered biosynthesis pathways that use methyl halides as a methyl donor.

From non-specific methylation of halides by methyl transferases

Higher plants contain a variety of different *S*-adensoyl-methionine (SAM)-utilizing methyltransferases. Algae and fungi both contain SAM-utilizing methyltransferases and produce a variety of secondary compounds including polyketides, phenolics, isoprenoids, steroids and alkaloids. It is possible that these enzymes catalyse the methylation of halides because the ubiquitous halide ions may easily intercalate into the active site of methyltransferases (Manley 2002). It has been speculated that volatile halogenated organic carbons may be formed by side reactions of these non-discriminating haloperoxidases or other peroxidases (Hewson & Hager 1980).

As a means of halide excretion

Krysell (1991) concluded that phytoplankton produce methyl halides for the elimination of toxic halogens from the cell and protection from herbivore feeding. It has also been proposed that marsh plants regulate tissue halide levels and excrete excess halides through the production of methyl halides (Ni & Hager 1999). However, this is countered by Manley (2002) who points out that in the case of chloride, the levels excreted are very small compared to the tissue halide levels, and less than the natural variability. This is also the case for chloride in Brassica (Gan *et al.* 1998), chloride in kelps (Manley & Dastoor 1987) and iodide in kelps (Manley & Dastoor 1988). It is unlikely that methyl halide production is used as a means of maintaining halide levels in the organism as a whole, but may be useful for halide regulation at a very localized scale. A methyl transferase compartmentalized in small membrane vesicle in these plants could maintain a proper chloride level for the functioning of adjacent enzymes associated with this structure, however this remains untested (Manley 2002).

Protection

It has been suggested that the production of certain halogenated compounds provides protection from herbivores, epiphytes or bacteria, but no strong link is shown for the methyl halides. Volatile halogenated organic compounds (VHOC) may provide protection from herbivore feeding or have antimicrobial benefits (Fenical 1975; Hewson & Hager 1980). CH_2I_2 was found to be present in some algae avoided by periwinkles (Gschwend *et al.* 1985). The seasonal cycle of epiphyte microflora on a seaweed was found to be related to algal metabolism (Sieburth & Tootle 1981), and it was speculated that volatile halogenated compounds used as antibiotic epiphytic control were involved in this seasonal cycle (Gschwend *et al.* 1985). Krysell (1991) also speculated that methyl halides could be for protection from herbivore feeding, as well as for eliminating halogens from the cell. However, no strong causal link has been demonstrated.

As a pheromone

Fenical (1975) suggested the role of methyl bromide could be as an antifouling control and an antimicrobial compound, and also function a pheromone used in sexual reproduction. This has not been confirmed by any research since.

For extra-cellular structures

Bromine is involved in certain extra-cellular secretions including some with known haloperoxidase enzymes. There is a possibility that methyl bromide could be involved as a carrier or intermediary in these processes. Assembly and adhesion of extra-cellular stalks of diatom *Achnanthes longipes* is dependant on bromide and is inhibited by iodine (Johnson *et al.* 1995). There is some cytochemical evidence that peroxidase activity occurs within intracellular vesicles in *A. longpipes* cells and that bromide-dependant, peroxidase-mediated phenolic cross-linking of extracellular adhesive polymers occurs (Wustman *et al.* 1997).

1.9 Iodine, particles, clouds and climate

There is a mechanism of new particle formation in the MBL through the nucleation of iodine oxides from biogenic precursors (O'Dowd *et al.* 2002b). There are also

other biogenic emissions from the coast that possibly lead to particle formation, and one aim of this research thesis is to investigate this in the Cape Grim region. Some background regarding particle formation is given here for context.

1.9.1 Cloud formation

In the atmosphere pure water vapour can reach saturation levels of 400% or more and can be super-cooled below 0 °C before it will spontaneously coalesce back into droplets of liquid water. Droplets form far more readily on a non-gaseous surface. In the atmosphere this surface is provided by a solid particle in the form of a condensation nucleus, or 'seed'. Particles suspended in the air are termed aerosols since they are a suspension of solid particles in a gas phase fluid. The particles that are of the required size and nature to act as a point of nucleation for water vapour are called cloud condensation nuclei (CCN). The physical chemistry of CCN can be found in texts such as Finlayson-Pitts & Pitts (1999).

The conversion from water vapour to liquid rain droplets occurs on a sub micrometre scale. Aerosol that can act as CCN are typically between 0.1 μm and 1μm in diameter, and the cloud droplets that coalesce on them are typically 20 μm in diameter. Through various processes, cloud droplets grow in size until they are pulled by gravity to fall as rain. A typical rain droplet is 2 mm in diameter or larger. See Figure 1.11 for a visualization of the relative sizes of these particles and droplets.

The typical density of CCN in marine air is 100-1000 cm^{-3}. Particles come from a variety of sources, and contain a variety of compounds. There are two distinct origins of CCN aerosol, the first is the direct input of aerosol into the atmosphere (primary aerosol) such as soot, dust, clay and sea salt. The second is the formation of new aerosol in the atmosphere from precursor gases (secondary aerosol). Newly formed particles from gaseous precursors are typically small, in the nanometre scale, and need to undergo growth into the CCN size range before they can seed clouds. There are numerous processes of cell growth, involving numerous chemical species.

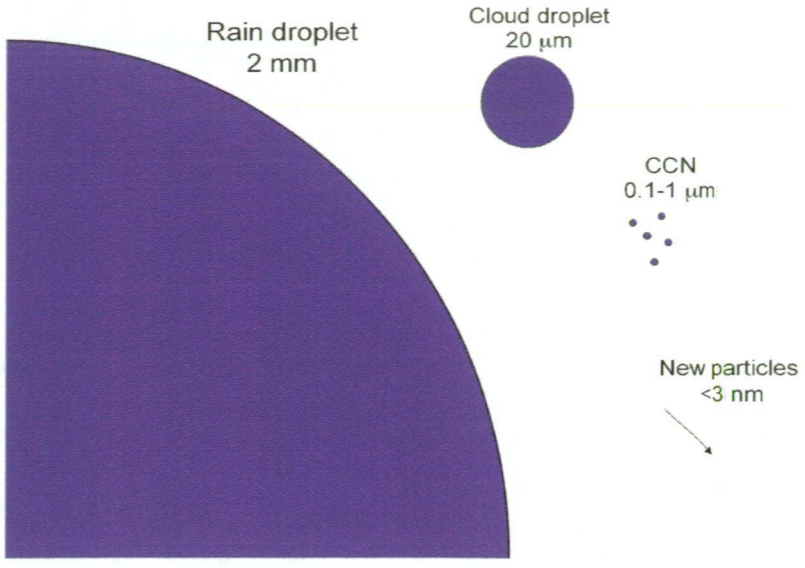

Figure 1.11 Relative sizes of natural raindrops, cloud droplets, Cloud Condensation Nuclei (CCN) and new particles (invisible at this scale)

1.9.2 New particle formation

There are two steps in the conversion of material from gas phase to stable solid particles. Firstly, a critical embryo or thermodynamically stable cluster of the order of 1 nm in size is formed from the coalescence of precursor vapours (Korhonen *et al.* 1999). Then, these stable clusters grow rapidly by coagulation and/or condensation to quasi-stable particles of 3-4 nm, before colliding by diffusion with larger, pre-existing particles (Kulmala *et al.* 2000). They are then subsequently captured, and the diameter increases.

There are numerous gases that act as precursors to new particle formation. In the marine context, sulfur can be transported from the ocean to atmosphere as DMS, where it is oxidized to various sulfur compounds such as sulfur dioxide, DMSO, dimethyl sulfonic acid and sulfuric acid, and contributes to sulfur aerosol. There are also iodine precursor compounds emitted from the ocean and coast that can act precursors to new particle formation. Organic compounds such as isoprene may also act as precursors to new particle formation (Meskhidze & Nenes 2006).

1.9.3 Production of particles from iodine precursors

Iodine is a precursor to new particle formation through a complex pathway resulting in particles of iodine oxide (O'Dowd *et al.* 2002b). This pathway was suggested after high levels of iodine oxides IO and OIO were found in the MBL at coastal sites (Alicke *et al.* 1999, Allan *et al.* 2000, Allan & Plane 2001). Further evidence of the role of iodine was the observation that iodine is often enriched in marine aerosols by 2 to 3 orders of magnitude compared with its relative abundance in sea salt (Vogt *et al.* 1999) often in the form of iodate (IO_3^-). This enrichment can be an order of magnitude higher in fine aerosol compared to the coarse mode, and is often associated with a depletion of bromine and chlorine (Baker 2004). This suggests that iodine is primarily involved in the formation and growth of new particles, rather than the secondary growth of new particles into CCN size.

Iodine in aerosol was first observed at the Mace Head research station in Ireland. At this site, there are extensive beds of Oarweed (*Laminaria digitata*), which has exceptionally high iodine content near the station. Measurements at other locations with different conditions are sparse, therefore the global significance of new particles from an iodine origin remains largely unquantified (Burkholder *et al.* 2004).

Studies at Mace Head initially indicated that a dominant pathway of new particle formation was through the emission of alkyl halides (CH_2I_2, CH_2ICl, CH_3I) from the kelp beds and ocean that undergo photolysis to produce I atoms and then IO by reaction with O_3 (e.g. Carpenter *et al.* 1999; Alicke *et al.* 1999). Rapid cycling of iodine compounds through sea salt particles back to gas phase was proposed to maintain the concentration of IO (Vogt *et al.* 1999), and laboratory experiments demonstrated the process occurred under a range of conditions down to near atmospheric levels of CH_2I_2, ozone and radiation (Hoffman *et al.* 2001; Jimenez *et al.* 2003; Burkholder *et al.* 2004). However, other studies have indicated that the source of alkyl halides whilst significant, is not sufficient to explain new particle bursts (McFiggans *et al.* 2000; Jimenez *et al.* 2003), or is only significant in areas of elevated CH_2I_2 leading to "hot spots" of IO and OIO concentration (Burkholder *et al.* 2004).

Smog chamber experiments combined with observations from Mace Head provided evidence that emissions of elemental iodine (I_2) could be the primary source (McFiggans *et al.* 2004; Saiz-Lopez & Plane 2004, Saiz-Lopez *et al.* 2004, 2005; O'Dowd & Hoffman 2005). Iodine from emissions of I_2 at low tide has been found to provide a source of I^- about 10^3 times greater than from CH_2I_2 (McFiggans *et al.* 2004). Iodine (I_2) released from kelp at low tide is rapidly photolysed by ultraviolet light to I atoms. Chamber experiments using natural atmospheric conditions and realistic biomass loadings in a flow-through design to create a steady state experiment showed correlations between I_2 and biomass as well as between I_2 and particles (Sellegri *et al.* 2005). This correlation provides evidence of a direct I_2 vapour source, which is supported by modeling work (Pirjola *et al.* 2005). Analysis of different measurements and modeling outputs shows that the iodine species associated with this process are concentrated over a short distance (a few hundred metres) over the intertidal zone (Saiz-Lopez *et al.* 2005).

Whatever the source of iodine, whether from I_2 emissions or organic iodine gases, the I^- ions react rapidly with ozone (O_3) to form IO. Self-reaction of IO then forms OIO and I_2O_2 (Cox *et al.* 1999). IO and OIO are then removed from the gas phase by uptake onto pre-existing aerosol surfaces, or initiate new particle formation by forming higher oxides I_2O_X where x = 2-5 (McFiggans *et al.* 2000; Hoffman *et al.* 2001; O'Dowd *et al.* 2002 a, b; Jimenez *et al.* 2003; Burkholder *et al.* 2004; Saunders & Plane 2005). A summary of the hypothesized chemical reactions resulting in new aerosol associated with the precursors from organic iodine gases is shown in Figure 1.12.

New particle formation events from iodine at Mace Head were strongest in spring and autumn, lowest in winter, and are statistically correlated with low tide height and solar radiation (Yoon *et al.* 2006). Events typically started ~75 minutes before low tide and the intensity was correlated to tidal area exposed at low tide and low tide height (Yoon *et al.* 2006).

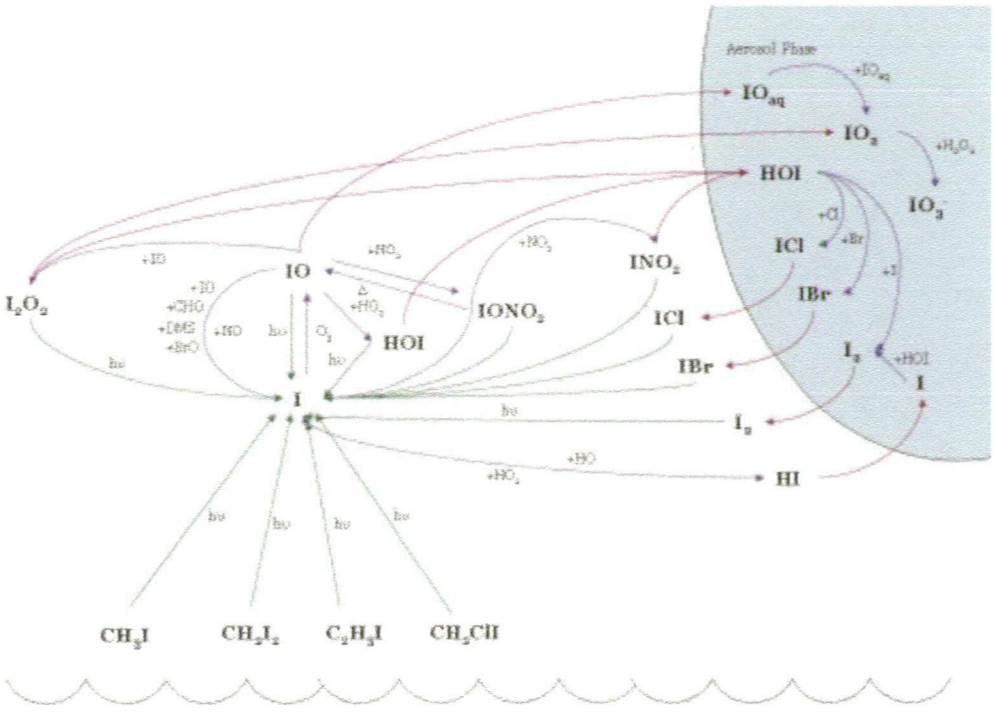

Figure 1.12 A schematic of the hypothesized processes associated with iodine from biologically produced organic iodine gases from the ocean resulting in new particles of iodine oxide. Green arrows indicate photolysis, blue arrows indicate reactions and red arrows indicate change of phase (source: Carpenter homepage 2007 http://www.york.ac.uk/depts/chem/staff/ljc.html)

The region around Mace Head, and in particular the beds of *Laminaria* kelp, are known to emit high concentrations of iodine. This may be an atypical site, and similar conditions may not commonly be present at other locations, including Cape Grim. In many coastal sites, the concentrations may be far lower than the required threshold for direct processes of new particle formation: 10 pptv for I_2 (Saiz-Lopez & Plane 2004), and 15 pptv for CH_2I_2 (Jimenez *et al.* 2003). However, iodine may be involved in other reactions. For example interactions between iodine and sulfur species have been hypothesized (Chatfield & Crutzen 1990) and IO is an efficient oxidizer of DMS (Nakano *et al.* 2003). Models show that the oxidation of DMS by halogens including BrO is significant and results in more particulate sulfur (von Glasow & Criutzen 2004).

1.9.4 Ocean-atmosphere cycles and feedbacks

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A global-scale feedback between the ocean and atmosphere has been proposed through the emission of DMS produced by phytoplankton, named the CLAW hypothesis. It has also been suggested that there may be some contribution to this feedback loop by open ocean emission of biogenic iodinated gases (e.g. Smythe-Wright *et al.* 2006).

Cloud and aerosol over the ocean affect the global radiation budget through the scattering of light and can also affect the UV light flux. Changes to the chemistry and size distribution of aerosol cause changes to the radiative forcing of the global climate. The CLAW hypothesis proposes that phytoplankton that produce DMS respond to climate forcing forming a negative feedback loop that acts to stabilize the temperature of the Earth's atmosphere (Charlson *et al.* 1987). The hypothesis was proposed by Charlson, Lovelock, Andreae and Warren, and takes its name from the first initial of their surnames.

Since oceans cover a large proportion of the Earths surface, marine clouds are of particular importance to global climate. Also, there is less effect to marine clouds from anthropogenic aerosol or precursor gases compared to on land. CCN from a terrestrial source can be transported long distances out to sea and be important to marine clouds, however there is still a large proportion of the earths surface that is unaffected by terrestrial aerosol, particularly in the southern hemisphere.

The CLAW hypothesis describes a loop where phytoplankton growth responds to the input of light to the ocean through the physiological effect of light and temperature. Increased light leads to increased phytoplankton growth, including those taxa that synthesize DMSP such as coccolithophorids. Increased DMSP leads to increases in its breakdown product DMS, which can then move from the ocean to atmosphere where it is oxidized to form sulfur dioxide, leading to increased sulfate aerosols. These aerosols act directly and through action as CCN to reduce light to the ocean, closing the loop.

The significance of the presence of a feedback loop is that the effect of changes to the climate system through increased or decreased solar input is counteracted and damped. This implies the feedback loop is part of a planetary-scale homeostasis.

However, the role of DMS and the presence of a feedback loop have been difficult to prove either from a theoretical or observational viewpoint. The theory of the processes controlling marine aerosol particle formation is not simple and is poorly understood. The CLAW hypothesis has gained some support from some subsequent observational work (Andreae *et al.* 1995, Cropp *et al.* 2005), but not all work supports it. It has been suggested that while a feedback may exist, it is weak since biogenic CCN only make up ~30% of total CCN, and is especially weak in areas with a significant influence from continental aerosol and is becoming increasingly weak due to the increase of anthropogenic aerosol (Vallina & Simo 2007). Other studies have suggested a feedback loop without a biological component (Shaw *et al.* 1998). The basis of the feedback being solely through DMS has also been questioned. Nucleation by the DMS mechanism is at a ternary H_2SO_4-H_2O-NH_3 nucleation site and simulations of this nucleation have shown that nucleation of thermodynamically stable clusters can readily occur under typical atmospheric conditions, but production of new particles via growth by vapour condensation is unlikely due to insufficient supply of H_2SO_4 (Pirjola *et al.* 2000). Therefore, the H_2SO_4 derived from the oxidation of DMS produced by phytoplankton can produce stable clusters but other vapours are needed to complete the process of new particle production.

The idea of a feedback loop between the ocean and atmosphere that includes a biological component to mediate climate forcing remains a very enticing idea, and work continues in the field. Feedback cycles involving other biogenic vapours have also been examined, including through the production of secondary aerosol from isoprene over the Southern Ocean (Meskhidze & Nenes 2006).

1.10 This study

This research thesis examines the sources and sinks of the methyl halide gases (methyl bromide and methyl iodide) from the ocean that affect the concentrations measured at the Cape Grim station. Specific aims of this study regarding this marine source of these gases were outlined in Chapter 1.2 (Aims and scope). To pursue these goals, the time series of methyl halide concentration measured at the Cape Grim station were analysed (Chapter 2) then a series of field measurements was conducted in each marine methyl halide source region relevant to Cape Grim. These areas comprised the open Southern Ocean (Chapter 3), the coastal waters of northwest Tasmania (Chapter 4) and the inshore waters less than 5 km offshore, including kelp beds (Chapter 5).

Since iodine gases can act as precursor compounds to new particle formation, the particle concentration measured at Cape Grim station was examined (Chapter 2). A comparison between periods of elevated emission of iodine gases at the coast and particles detected at the station was also conducted (Chapter 6).

Chapter 2. Analysis of methyl halide and particle concentrations measured at the Cape Grim station

2.1 Introduction

A time series of methyl bromide and methyl iodide concentrations collected under the AGAGE at Cape Grim program are presented here. Cape Grim Baseline Air Pollution Station (CG-BAPS) is at the northwest tip of Tasmania (40.68 °S, 144.69 °E), at the top of a sea cliff (94 m elevation) less than 100 m from the coast. Air arrives at the station from various directions, but only 'baseline' air was considered here. Baseline is defined as air that arrives from over the marine upwind fetch zone (see Figure 1.4, Chapter 2.2.6). This fetch zone includes a large area of the open Southern Ocean and Indian Ocean, as well as shelf and coastal waters of northwest Tasmania and the inshore environment immediately in front of the station. Each of these areas was expected to contain sources and sinks of methyl halides that influence the measurements made at Cape Grim. The AGAGE time series gives context to the measurements made in the open ocean, coastal waters and shore at Cape Grim presented in subsequent chapters.

Connections between the seasonal and daily cycles of the methyl halides and variables measured in the open ocean were examined. To investigate links between the station data and the broad scale ocean processes, satellite ocean data were examined. Connections between the timing of events of elevated concentration of methyl halides at the station and variables measured in coastal were also analysed. To examine the coastal processes related to tidally exposed kelp beds, tide data was also examined. Additionally, to examine the bursts of new particles from biogenic precursors emitted from the ocean, the small particle record was also examined.

2.2 Methods – data sources & filtering

2.2.1 Methyl bromide

In situ measurements of methyl bromide were made at Cape Grim from 1998 to 2004 using an automated adsorption-desorption system (ADS) coupled with gas chromatography with mass spectrometry (GC-MS; Sturrock *et al.* 2001, Prinn *et al.* 2000, Cox *et al.* 2003). Measurements of methyl bromide have been made since January 2004 using the 'Medusa' GC-MS instrument that features improved accuracy and calibration (Miller *et al.* 2006). Details of the instrument, columns and calibration are given in the above publications.

An analysis of the record from 1998 to 2001, including identification of source regions, is presented in Cox *et al.* (2005). Methyl bromide concentration in baseline air averaged 8.07 ± 0.55 pptv, which is lower than other southern hemisphere measurements from ships cruises by typically 1-2 pptv but up to 6 pptv (Cox *et al.* 2005). The average for summer was 7.44 ± 0.69 pptv, and in winter was 8.03 ± 0.38 pptv, with no strong annual cycle, shown in Figure 2.1. Using back-trajectory analyses, elevated events were identified from coastal-terrestrial and coastal-seawater sources from Tasmania and Victoria as well as industry in Melbourne.

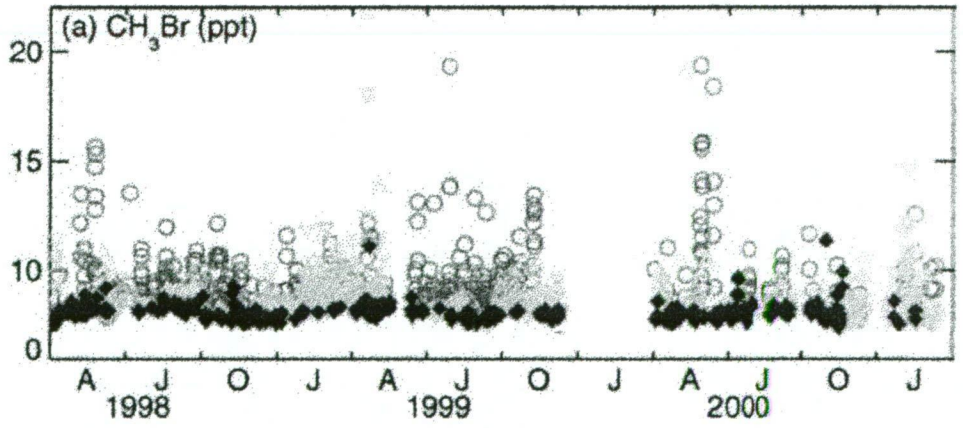

Figure 2.1 Measurements of methyl bromide at Cape Grim in 1998-2001 (cirlces- non-baseline air; pale diamonds- baseline rejected after filtering; dark diamonds- baseline air, source: Cox *et al.* 2005)

2.2.2 Methyl iodide

Measurements of methyl iodide in air at Cape Grim were made periodically during the 1980s. Methyl iodide concentration in marine air at Cape Grim was 2.4 ± 1.3 pptv in 1981 (Rasmussen *et al.* 1982a, b). Methyl iodide has been measured routinely at the Cape Grim BAPS station since early 1998. Early measurements in 1998-1999 were made using GC-MS in the AGAGE program and are reported in Cohan *et al.* (2003). A set of measurements was then made on the ADS GC-MS system described above (Sturrock *et al.* 2001), and an analysis of this data is found in Cox *et al.* (2005). Measurements show poor agreement between these two systems by a factor of three. Since 2003, measurements have been made using the 'Medusa' GC-MS instrument.

The GC-MS measurements reported in Cohan *et al.* (2003) do not calibrate with later measurements, but trends in the data are still noteworthy. In 1998 and 1999 methyl iodide showed a seasonal cycle peaking in summer. This suggests oceanic emissions were 2.2 to 3.6 times stronger in summer than in winter once photolytic loss is accounted for (Cohan *et al.* 2003). Back trajectories show the highest source regions were the Tasman Sea and Bass Strait and the lowest were from the Southern Ocean at higher latitudes (Cohan *et al.* 2003).

An analysis of ADS GC-MS measurements from 1998-2001 (Cox *et al.* 2005) showed similar trends. Back trajectory analysis indicated that coastal-terrestrial and coastal-seawater sources from Tasmania and Victoria were a significant source of methyl iodide. The coastal wetlands at Corner Inlet in southern Victoria were a major source region and sources from Bass Strait were greater than from the open ocean. Baseline measurements from a clean marine origin showed an average of 1.41 ± 0.41 pptv with a seasonal cycle (Figure 2.2). There was a higher concentration and greater variability in summer (1.62 ± 0.93 pptv) and lower concentration and less variability in winter (1.30 ± 0.17 pptv).

The seasonal cycle in average concentration was described by a sinusoidal curve of amplitude 0.47 pptv. Since the photolytic loss term is expected to be much greater in summer, this means that the source term must be relatively much greater to account for the summer maximum. This annual cycle was attributed by Cox *et al.* (2005) to a

correlation with sea surface temperature (SST) indicative of a photochemical production of methyl iodide in surface seawater, after Yokouchi *et al.* (2001).

There is also a seasonal cycle in variability in the measurements, with greater variability in summer. A lot of this variability is in the form of anomalous peaks above the normal range, especially in summer (Figure 2.2).

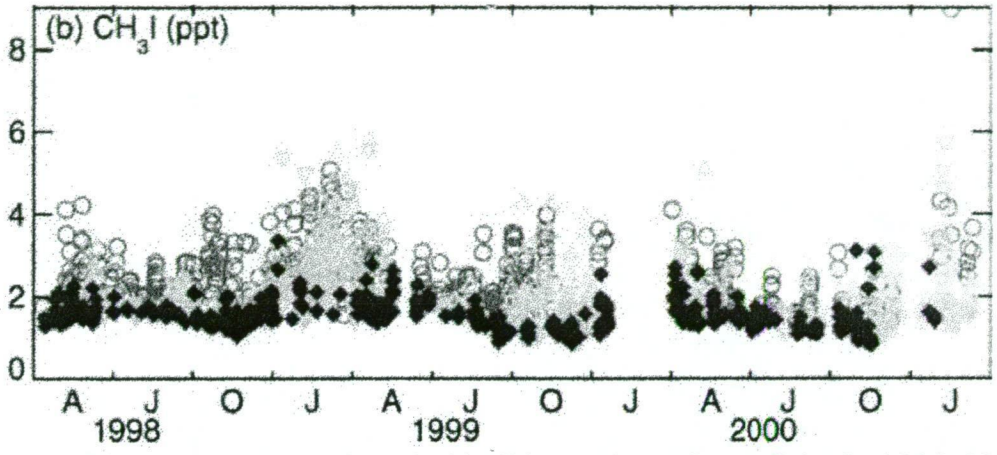

Figure 2.2 Measurements of methyl iodide made at Cape Grim in 1998-2001 (cirlces- non-baseline air; pale diamonds- baseline rejected after filtering; dark diamonds- baseline air, source: Cox *et al.* 2005)

2.2.3 Particles

Particle concentrations of various size ranges in air from the inlet 10 m above the ground have been measured continually using TSI instruments (TSI Corporation, USA) at Cape Grim for many years as part of the particles program (e.g. Gras 2004). Ultrafine condensation nuclei (UFCN) with a diameter 3 nm and greater have been monitored using a TSI 3025a UFCN counter, condensation nuclei (CN) with a diameter 11 nm and greater have been monitored using a TSI 3010 CN counter. Particle concentrations for both size ranges have shown a pronounced annual cycle with a summer concentration maximum and winter minimum (Gras 2004). The difference between the two particle counts can be used as an independent and continuous measurement of new particles (Jimi *et al.* 2003).

2.2.4 Ocean data

To examine the links between the concentration of methyl halides, particles and the processes in the marine source regions, oceanographic variables from MODIS 2.1 and SeaWiFS satellites and modeled productivity were examined (obtained from Oregon State University Ocean Productivity project 2007). These are surface Chlorophyll *a*, sea surface temperature (SST) and cloud-corrected photosynthetically active radiation (PAR). Net primary productivity (NPP) modeled using the vertically generalized production model (VGPM) of Behrenfeld & Falkowski (1997) based on Chlorophyll *a*, sea surface temperature, PAR light and an estimated euphotic zone depth.

These variables were examined in two regions in the baseline sector of the Cape Grim wind profile (Figure 2.3). Variables are area-averaged over one of two boxes, and also time-averaged to a monthly value. The larger Box 1 represents a significant area of the upwind fetch region of the station, in the 'roaring forties' region of latitude (40-50 °S, 110-140 °E). Box 2 represents the coastal waters surrounding the station and to the near south (41-42 °S, 144-145 °E). The figure shows an example back-trajectory of air arriving at the station from across the ocean.

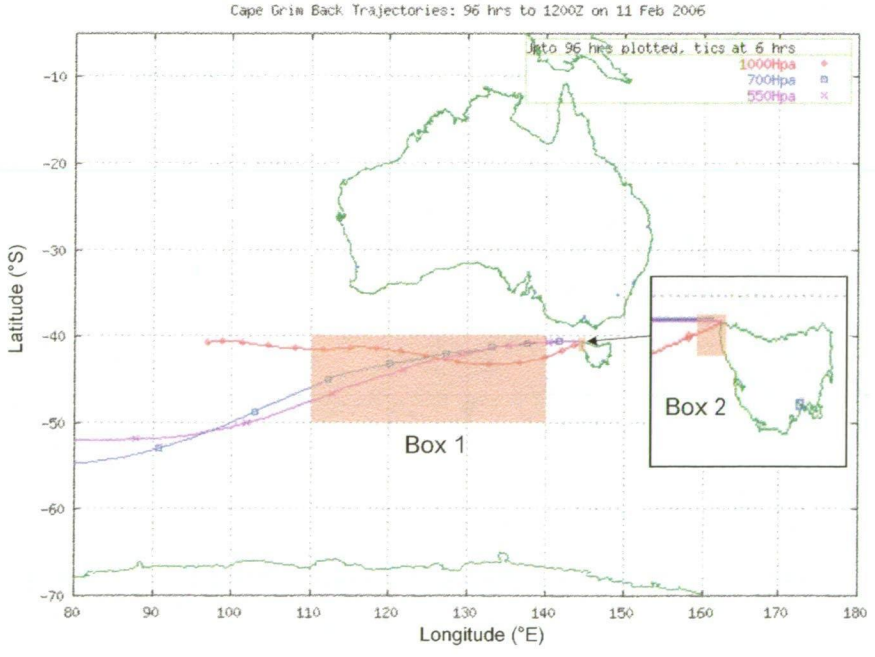

Figure 2.3 Wind back trajectory analysis for midday 11th February 2006 showing air mass 4-day back trajectories, also shown are the position of the two boxes used to calculate area averages of oceanographic variables from MODIS and SeaWiFS satellite data

2.2.5 Tide data

Tides are complex in the Cape Grim region since it is at the corner of the Tasmanian landmass and there is a steep gradient of lunar tidal forcing around this corner, which creates a gradient in tidal timing and tidal range (Figure 2.4). Tide data was obtained from the National Tide Centre (2007). There has never been a tidal gauge installed at Cape Grim; the nearest permanent tide gauge is at Stanley 50 km to the east of Cape Grim, facing onto Bass Strait. There was also a temporary gauge installed at Stack Island 10 km northeast of the station for a limited time between 1900 and 1910. The predicted tide for this location shows a slightly reduced range and later timing (40 minutes) than the Stanley gauge.

Since the tide in this region is complex and the tidal range and timing differs between Cape Grim, Stanley and Stack Island, a new measurement of tide was made at the Cape Grim station in November 2007. To measure tidal height, a Conductivity, Temperature and Depth (CTD) sensor was mounted securely in water approximately one metre below low tide directly in front of the station for 48 hours. Tidal range was smaller and tide timing was later than at either Stanley and Stack Island (Figure 2.5). The average tidal range was calculated as 0.96 m, and a maximum range of 1.45 m. To get tide height at Cape Grim, an offset in timing (1 hour) and height of tide (0.42) was applied to the values Stanley, as this is the nearest reliable gauge.

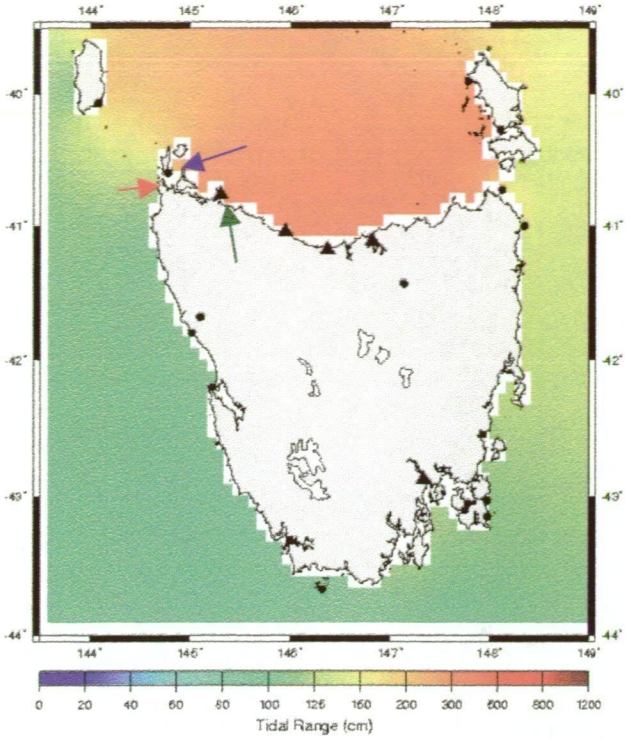

Figure 2.4 Tidal ranges in the waters surrounding Tasmania calculated from a tide model showing approximate locations of tide gauges and measurements, Red: Cape Grim, Blue: Stack Island, Green: Stanley (source: National Tide Centre 2007)

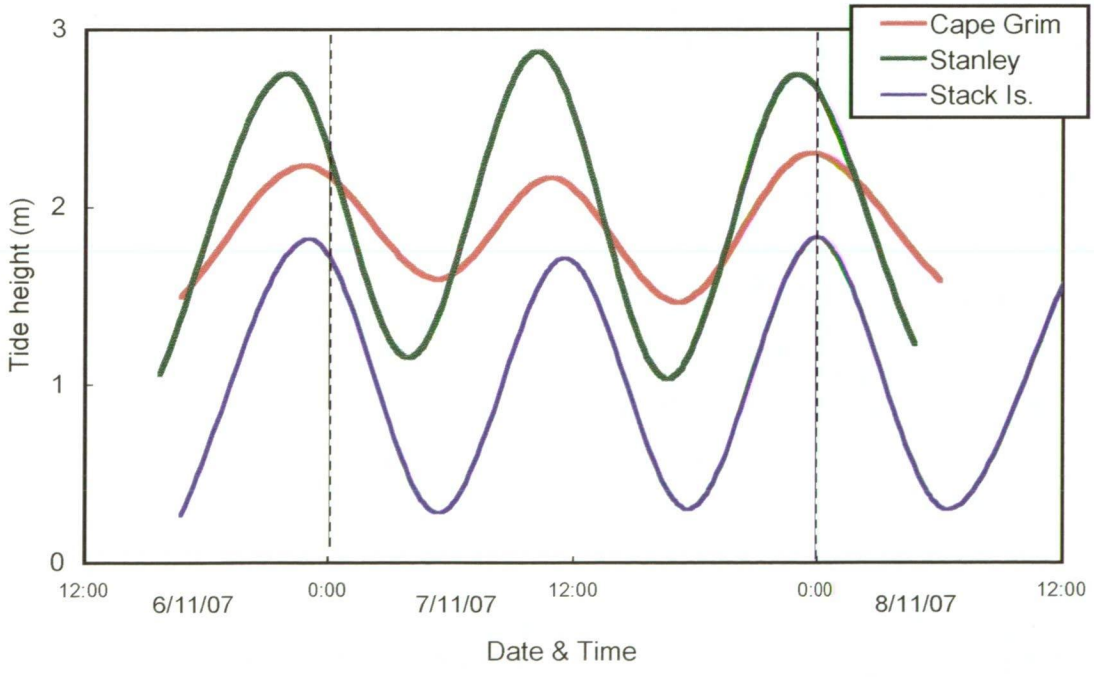

Figure 2.5 Tidal heights at the coast of northwest Tasmania: these measurements at Cape Grim, the permanent gauge at Stanley and the prediction for Stack Island based on measurements from a temporary gauge (source of Stanley and Stack Island data: National Tide Centre 2007)

2.2.6 Baseline filter

The focus of this study is the biogenic sources of methyl halides and precursor gases to new particles from a purely marine source. These sources are present in the open ocean, coastal waters, inshore environment and from beach-cast seaweed on the beaches near the station. The input from purely marine sources may be easily masked by intense terrestrial sources. For these reasons, a strict filter for establishing marine air must be applied. Clean air from the marine sector of the wind profile at Cape Grim is termed 'baseline' air. Several variables can be used to establish baseline including wind direction, wind speed, CN particle number, radon concentration, CO_2 concentration stability and modeled wind back trajectories. Some previously used baseline switches are shown in Table 2.1

The previous analysis of methyl halide data from Cape Grim (Cox *et al.* 2005) used a baseline switch outlined in Cox *et al.* (2003), which was based on wind direction 190 to 280 ° and the stability of carbon dioxide concentration. Any remaining data with high-frequency variability was then removed using a digital filter. High frequency variability may indicate the air is not well mixed and is therefore considered non-baseline for the purposes of that study.

A specialized filter was developed for this analysis to isolate measurements of air arriving at the station over the ocean, inshore waters and the beach from any air that has passed over land, while not filtering out short term peaks from local marine sources. First, a wind direction filter of 180-280 ° rather than 190-280 ° was applied to capture wind from the beaches to the south as well as the usual baseline sector. Air from this additional 10 ° sector that has passed over land was excluded during the next stage of filtering.

The data was then filtered using a radon concentration threshold to remove points with any terrestrial input. ^{222}Radon has a half-life of 3.825 days and is emitted as part of the decay chain from uranium (^{238}U), through radon (^{222}Ra) to lead (^{206}Pb). It is emitted almost exclusively from land surfaces and so is useful as an atmospheric tracer of contact with land (Zahorowski *et al.* 2004). Clean marine air has a low,

stable radon concentration of <60 mBq m^{-3}, compared to the high and variable concentration in continental air (>1000 mBq m^{-3}).

The radon filtering technique was suggested by Wlodek Zahorowski (Australian Nuclear Science & Technology Organization, *pers. comm.* 2007). The median concentration of radon was calculated in air measurements within each consecutive hour after local wind direction change into the baseline sector (190-280°), along with 10^{th} and 90^{th} percentiles. Radon concentration has been observed to stabilize within 12 to 24 hours after entering this wind sector, and this stable concentration can be taken as a marine air threshold. The calculated median radon concentrations from measurements made in 2004 to 2006 are shown in Figure 2.6. For these data, the median concentration between 24 and 48 hours was approximately 40 mBq m^{-3} and the 90^{th} percentile was 84.1 mBq m^{-3} (shown as dashed lines in Figure 2.6).

A filter of 84 mBq m^{-3} was applied to hourly averaged methyl iodide measurements. Following this, outliers were not iteratively removed and high frequency data was not digitally filtered out as was done by Cox *et al.* (2003), since anomalously high concentrations of methyl iodide and small particles may represent a local source from the inshore environment and beach and are an object of interest here.

Table 2.1 Conditions for baseline switches for Cape Grim atmospheric concentration (unpublished data)

Switch	Wind Dir.	Wind speed	CN	Additional conditions
BL 1	190-280°		<600	
BL 2	190-280°		<600	Manual switches
BL 3	190-280°		Seasonal	Manual switches
CO_2	190-280°			CO_2 concentration stable (±0.3 ppm over a 5 hour period)
BL FLAG for Lo-Flo instrument	190-280°	>5 m/s		CO_2 conc. stable, Smooth curve fit applied Outliers iteratively removed

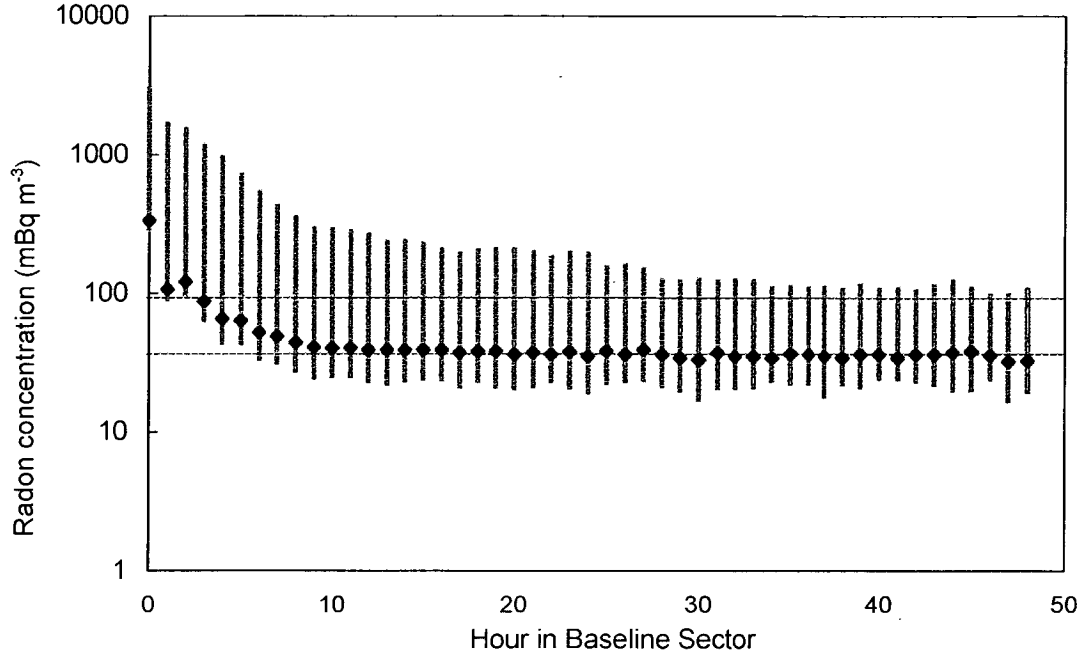

Figure 2.6 Median hourly concentration of radon in air at Cape Grim for 2004-2006 following a change of wind direction into baseline sector (190-270°), showing 10th and 90th percentile, dashed lines indicate the approximate position of stability of the median and the 90th percentile

2.3 Methyl Bromide

The Medusa instrument has a problem in the measurement of methyl bromide of drift in the primary standard air flasks from April 2005 onwards, and is currently in the process of reanalysis by AGAGE. For this reason, only data from January 2004 to May 2005 were analysed here (11,856 hours). Measurements were made at intervals of 2 hours and there are intermittent breaks for instrument calibration and repair, so the total number of measurements was 4,399. Data was then filtered by wind direction, reducing the number of points to 2,354, then filtered using the radon concentration threshold, resulting in 1,563 points.

2.3.1 Seasonal cycle

Since only 17 months of measurements are presented here, a recurring seasonal trend can't be confidently attributed to these data. However, the limited data suggests some temporal changes of small magnitude are present, which may prove to be part of a repeating seasonal cycle as the time series develops. The maximum monthly mean is 7.4 pptv in April, followed by a minimum of 7.1 pptv in July, giving a maximum change in monthly mean of 0.3 pptv (~4% of the total). The difference between the measured concentrations in these two months is significant (Student's T-test $p = 7 \times 10^{-22}$). The pattern found in the first 5 months of 2004 showed some indication of repeating in 2005 but with a lower magnitude.

These temporal changes are shown with a fitted interpolation spline (degrees of 20) in Figure 2.7a. The monthly means also show this trend (Figure 2.8). The temporal trend was not consistent with a fitted single sinosoid. However, when fitted with a sinusoid including the second component of a fourier sequence, the cycle is more accurately described, shown in Figure 2.7b. A seasonal cycle has not been detected in baseline air in previous years (Simmonds *et al.* 2004; Cox *et al.* 2005), but modeling work suggested that small seasonal changes should be present (Reeves 2003). The overall downward trend in methyl bromide concentration following the controls in the Monteal Protocol may disturb the detection of a seasonal cycle, especially within a time series this short.

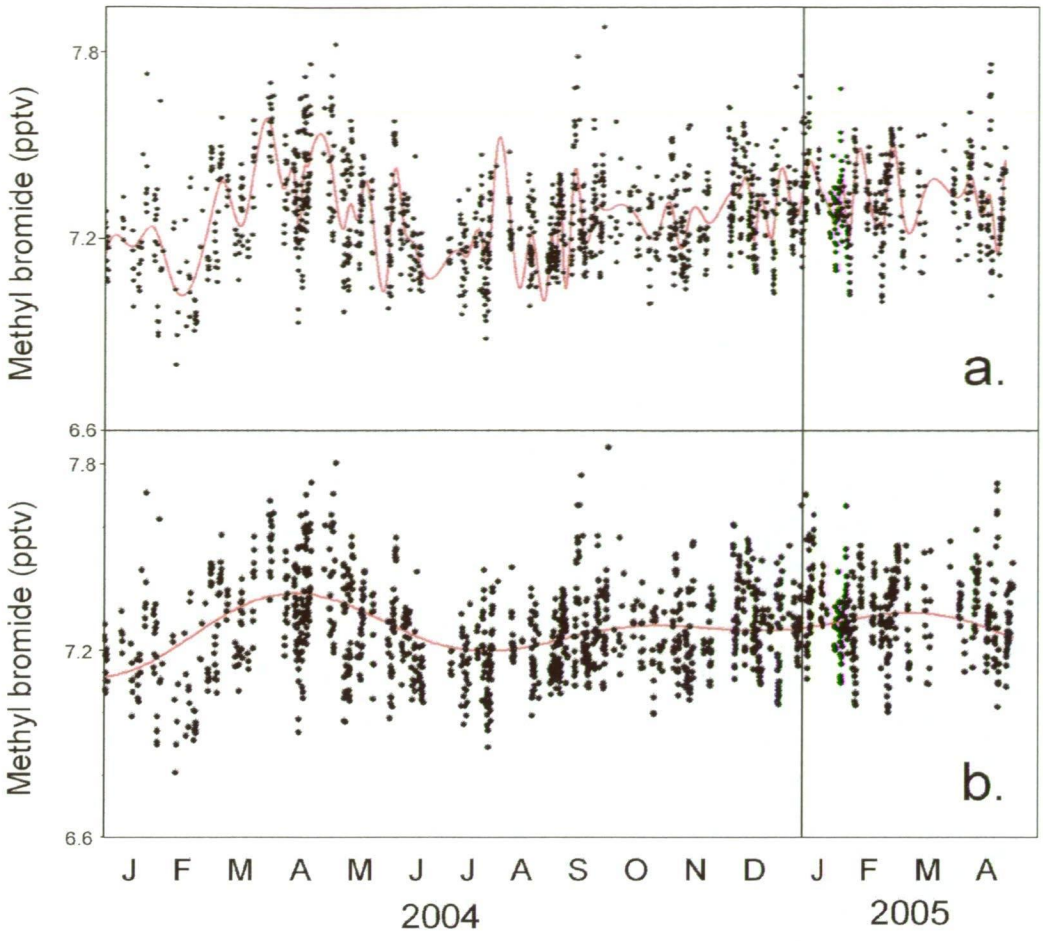

Figure 2.7 Methyl bromide concentration in baseline air at Cape Grim 2004-2005, with fitted (a) spline, and (b) sinusoid with 2 components of the fourier sequence

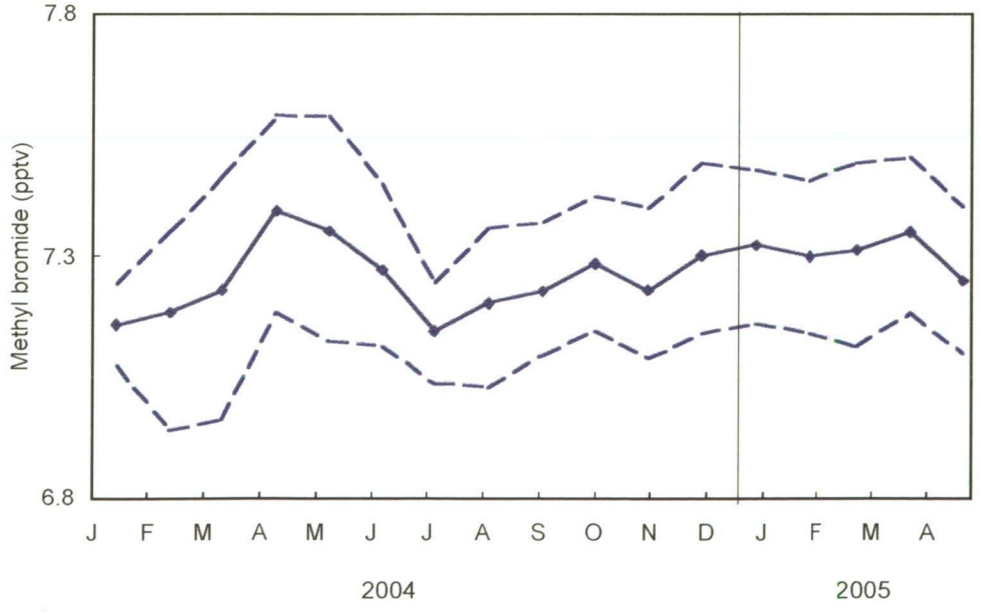

Figure 2.8 Monthly mean methyl bromide concentration in baseline air at Cape Grim for 2004-05, showing 10th and 90th percentiles

2.3.2 Comparison to ocean data

There is no obvious similarity in temporal changes in methyl bromide concentration and the ocean variables measured in the adjacent ocean in Box 1 (Figure 2.9, 2.10). The timing of the maximum in methyl bromide was not directly related to a peak of any ocean variable, coming two months after the peak in SST, and four months after the peak in PAR, Chlorophyll *a* and NPP. There are some similarities between the minima in PAR and NPP with methyl bromide in June and July, but this does not appear to be part of some consistent trend throughout the year. There was not only a lack of similarity in the timing of the peaks but in the basic shape of the time series.

The lack of a simple sinusoidal pattern of methyl bromide concentration in baseline air suggests there is no dominance of a single source or sink in the temporal trend. The temporal trend can be reasonably well described by a sinusoid with two components of a fourier sequence, suggesting there is a complex interaction of two or more out-of-phase sink and source terms, as proposed previously by Simmonds *et al.* (2004). To account for this interaction, the full range of sources and sinks would need to be accounted for, including the major atmospheric sink of reaction with hydroxyl radicals. Also, the influence of SST may be complex, since temperature passes above and blow the 16 °C threshold given by the King *et al.* (2002) equations (Equation 1.12a-d). The biological source may also be complex, and possibly have some time delay between peak NPP and methyl bromide emission, since phytoplankton can emit methyl bromide in the later stages of growth (e.g. Tokarczyk & Moore 1994, Scarratt & Moore 1998, Saemundsdottir & Matrai 1998). A more detailed analysis of the correlations between the variables is not included here, since the shortness of the time series would not allow for firm conclusions to be drawn. There was also some inter-annual variability between the January-April periods of the two years examined.

Since the compound has a lifetime of 0.7 years in the atmosphere (Orlando 2003), the oceanic source region that is represented in measurements at Cape Grim is much larger than the area of examined here in Box 1 shown in Figure 2.4. The source and sink terms from a much larger marine region and possibly terrestrial input from other southern hemisphere landmasses would be represented in the concentration of methyl bromide measured at Cape Grim.

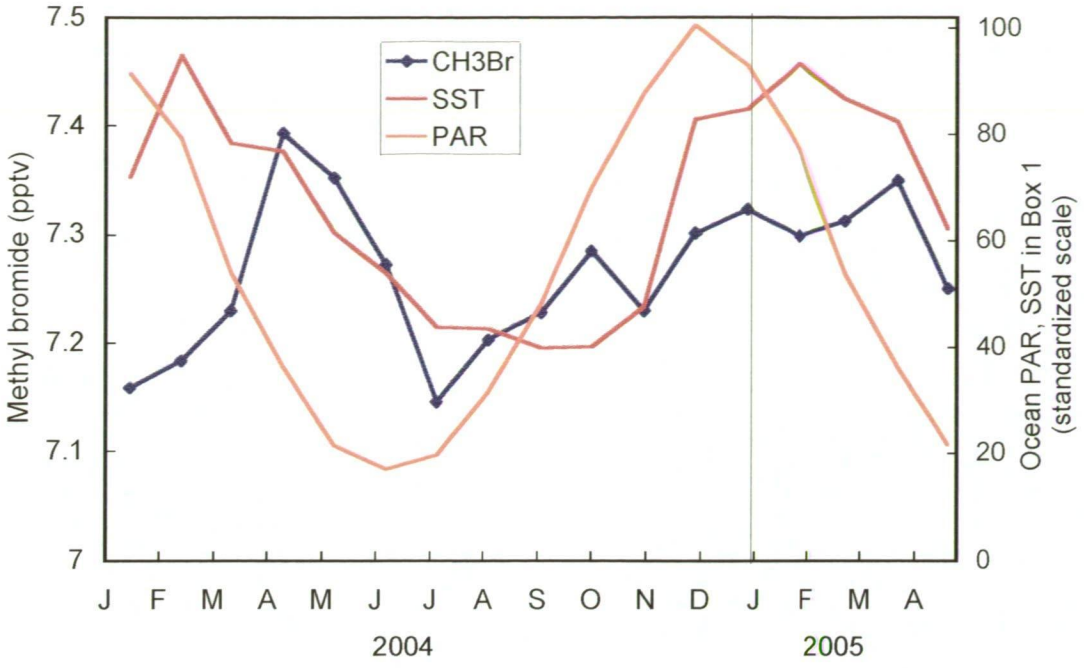

Figure 2.9 Monthly mean methyl bromide concentration in baseline air at Cape Grim, monthly mean sea surface temperature and photosynthetically active radiation in surface waters of the Southern Ocean (Box 1)

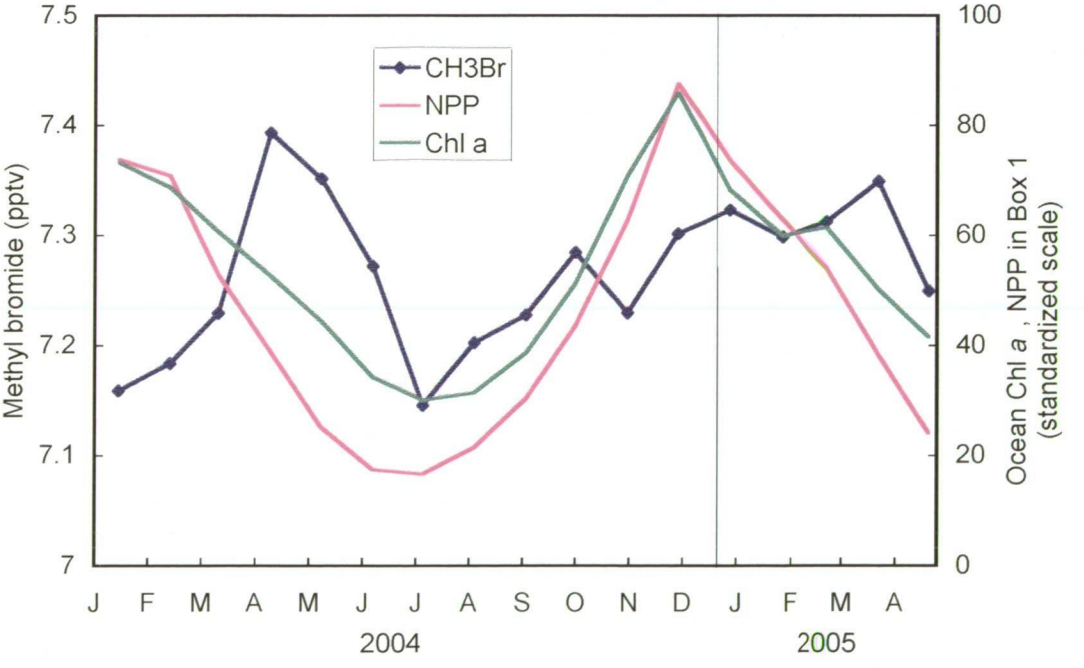

Figure 2.10 Monthly mean methyl bromide concentration in baseline air at Cape Grim, Chlorophyll *a* and modeled net primary production in surface waters of the Southern Ocean (Box 1)

2.3.3 Daily cycle

The difference between each methyl bromide concentration measurement from the monthly mean was calculated, and this anomaly was plotted against hour of the day of the measurement (Figure 2.11). No obvious trend in the anomaly is present with hour of measurement. To examine the source of elevated emissions of methyl bromide, the periods when the hourly mean methyl bromide concentration was >0.3 pptv above monthly mean were isolated. These represented 26 hourly measurements during 20 events. This threshold was decided from a qualitative inspection of the data, isolating the most distinct peaks of elevated concentration above the general range. There was no significant trend in either number of measurements or concentration in any hour through the daily cycle (Figure 2.12).

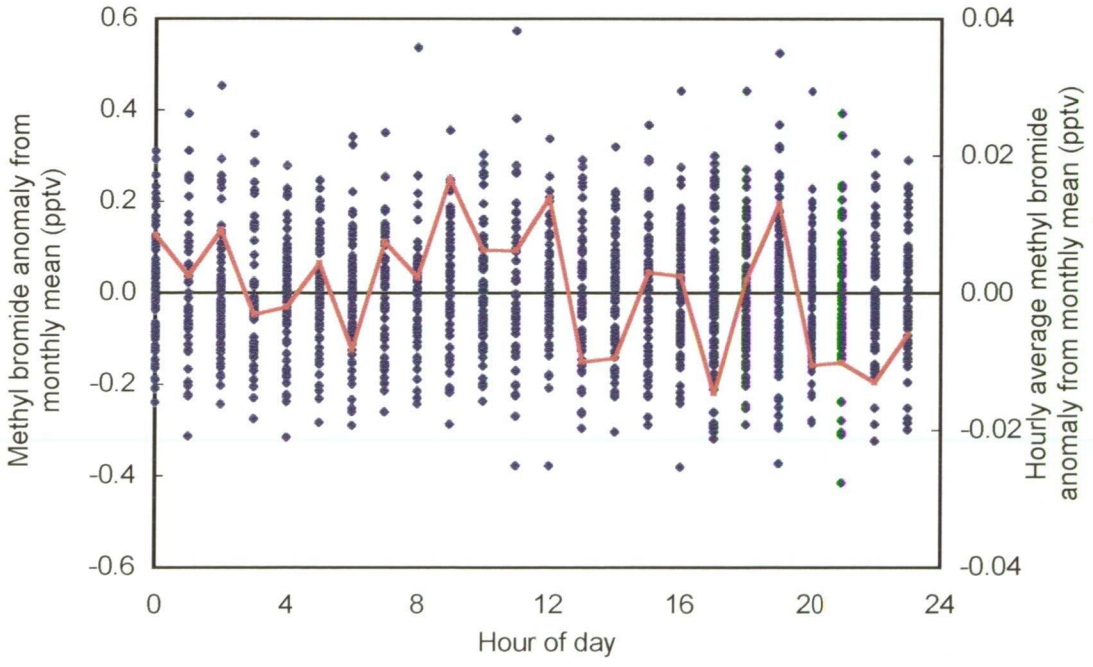

Figure 2.11 Methyl bromide in baseline air at Cape Grim: concentration anomaly from monthly mean with each hour of the day in baseline air and hourly average of this anomaly (red line)

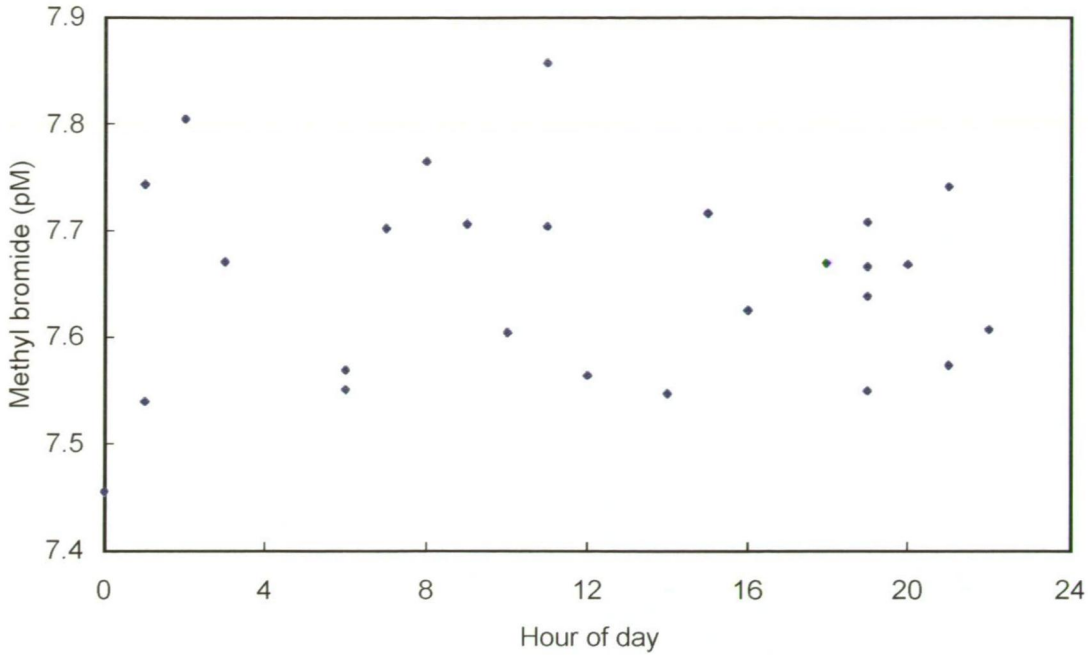

Figure 2.12 Methyl bromide measurements in baseline air at Cape Grim > 0.3 pptv above the monthly mean, plotted against hour of measurement

2.3.4 Coastal emissions

To investigate any source from blooms of phytoplankton in coastal waters, the timing and magnitude of the measurements > 0.3 pptv above the monthly mean are compared to the modeled Net Primary Production (NPP) in coastal waters in Box 2 (Figure 2.13). This comparison showed no strong trend, but further data are required to confirm any relationship.

To investigate any source from tidally exposed kelp beds, the timing and magnitude of the 20 events are compared to tidal cycle at Cape Grim. A typical plot is shown in Figure 2.14, with three elevated incidents on consecutive days (24-27 September 2004). There appears to be a positive correlation with tide height in some measurements, but not in others. It appears that there is no strong and reliable trend with tide height.

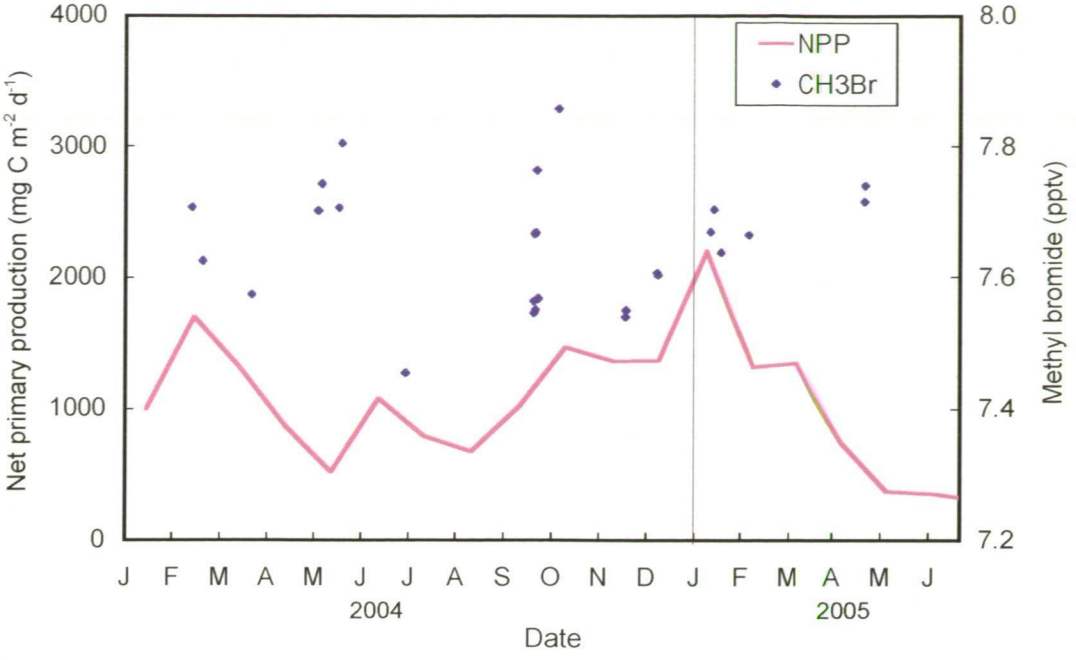

Figure 2.13 Net primary production modeled for Tasmanian coastal waters (Box 2), and methyl bromide concentration in baseline air in events >0.3 pptv above monthly mean

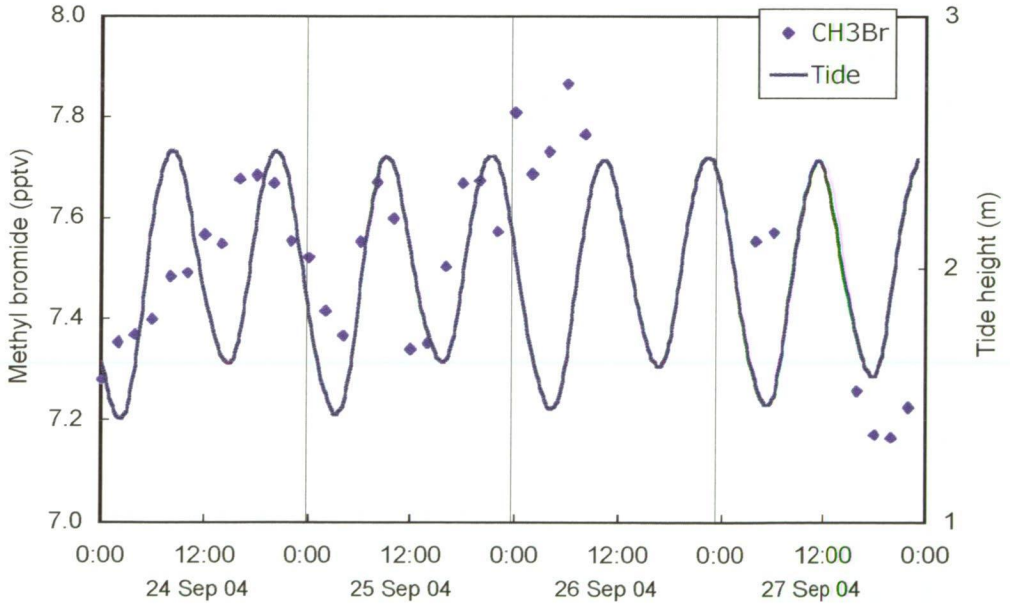

Figure 2.14 Estimated tide height and measurements of methyl bromide concentration in baseline air at Cape Grim, 24-27 September 2004

2.4 Methyl iodide

2.4.1 Seasonal cycle

Measurements from AGAGE taken between 1 January 2004 and 31 December 2006 are presented here (26,304 hours). Measurements were made at approximately 2 hourly intervals with breaks in the record for instrument maintenance, calibration and repair and a large section is missing from the record between September 2004 and March 2005. So the total number of measurements analysed here was 8,369. The use of the wind direction filter reduced the number of points to 4,101, and the radon filter further reduced the number to 2,850.

Methyl iodide concentration in baseline air is displayed in Figure 2.15, showing a repeating annual cycle with some inter-annual variation in this cycle. There is an approximately sinusoidal seasonal pattern, shown as a polynomial fitted curve calculated from all years' data. This is consistent with patterns found in previous years (Cox *et al.* 2005). The seasonal cycle is slightly later than calendar seasons, with a maximum in February to April of 1.62 ± 0.4 pptv, and a minimum in August to October of 0.91 ± 0.3 pptv. The maximum and minimum values from the fitted curve are 1.62 and 0.87 pptv respectively. These maximum is similar to the previously measured value of 1.62 pptv, but the minimum is lower than the previously measured value of 1.3 pptv (Cox *et al.* 2005). There is a corresponding reduction in the overall average concentration of 1.24 pptv, compared to 1.4 pptv, and an increase in the peak-trough amplitude of the sinusoidal curve, 0.75 pptv compared to 0.47 pptv in previous data (Cox *et al.* 2005). Differences in magnitude may be partly due to the use of a different instrument and a different filter.

Monthly means from all years are shown in Figure 2.16, including standard deviations as well as 10th and 90th percentiles. There are not only seasonal changes in the average, but also in variability. The measurements are more variable in summer, giving an increase in the standard deviations of monthly averages (Figure 2.16). This variability is mainly in the form of short-term peaks above the general range.

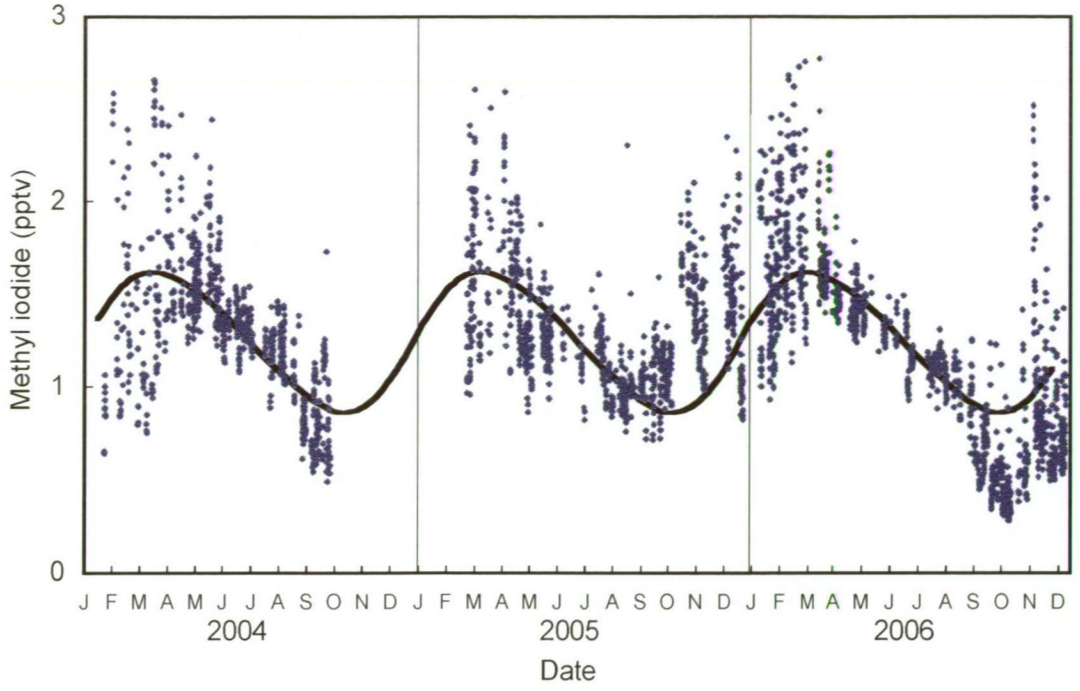

Figure 2.15 Methyl iodide concentration in baseline air at Cape Grim 2004-2006 and fitted sinusoidal trend line indicating seasonal cycle

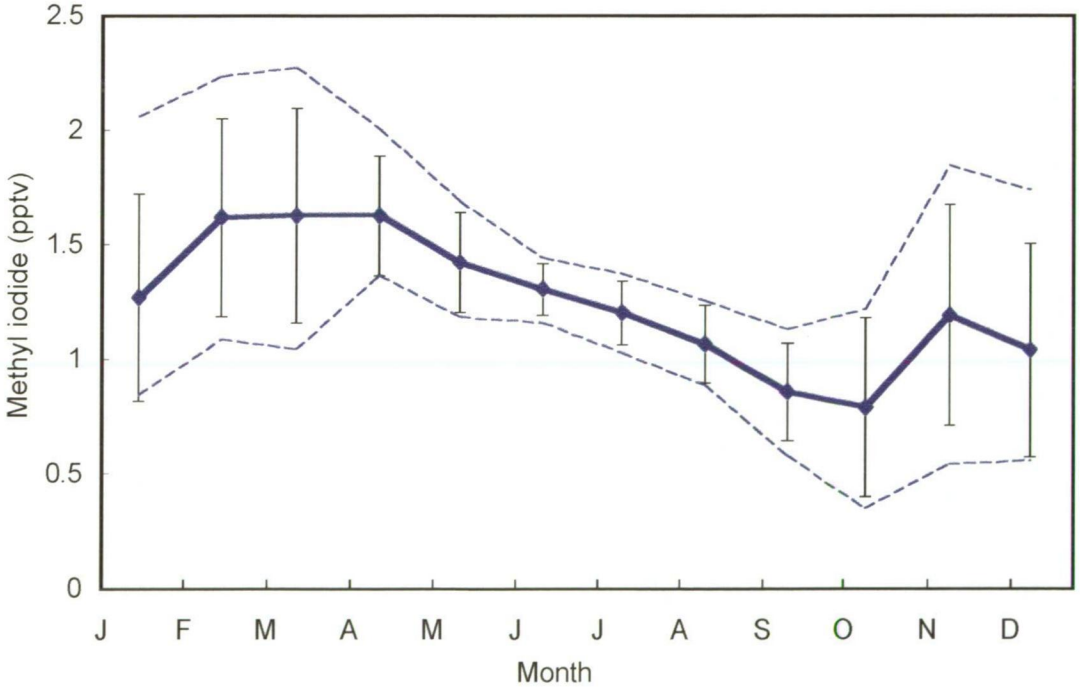

Figure 2.16 Monthly mean methyl iodide concentration in baseline air at Cape Grim 2004-2006, showing standard deviation (bars) as well as 10th and 90th percentiles (dashed lines)

2.4.2 Comparison to ocean data

The concentration of methyl iodide in baseline air measured at Cape Grim is the net result of all processes, including all sources, sinks and the air-sea flux rates. The seawater concentration is affected by the two marine sources, photochemical production and biological production in surface waters, and also by chemical processes that are temperature dependent. Flux rates between ocean and atmosphere are dependant on physical variables including wind and temperature. Once in the atmosphere, the main sink that affects the eventual detection of the concentration at the Cape Grim station is photolysis. These terms and processes are outlined in Figure 2.17, adapted from Hughes *et al.* (2007).

The biological source has many complexities, as discussed in Chapter 1. Factors affecting the biological source include the composition and biomass of the phytoplankton community, levels of stresses, grazing, state of senescence, as well the processes involving bacteria and within marine aggregates. For these reasons, the magnitude of the biological source may show some correlation to the phytoplankton biomass or primary production, but this correlation is not expected to be perfect due to the complexities of the processes.

In general, there has been found to be a strong correlation between the seasonal cycle of methyl iodide measured at monitoring stations and the sea surface temperature of the adjacent ocean. This correlation is present in records from the northwest Pacific, Hateruma Island and Alert station in far northeast Canada (Yokouchi *et al.* 2001), as well as the northwest Atlantic (Moore & Groszko 1999), Mace Head in Summer (Bassford *et al.* 1999) and Mace Head in Spring (Carpenter *et al.* 1999). Some of these correlations are immediately recognizable in the seasonal cycle in methyl iodide concentration measured at temperate monitoring stations shown in Figure 2.18. The seasonal cycle measured at Cape Grim also appears to be correlated with monthly average SST measured from SeaWiFS satellite data from Box 1 (Figure 2.19). Considering the numerous factors influencing methyl iodide concentration, this reasonable correlation is noteworthy.

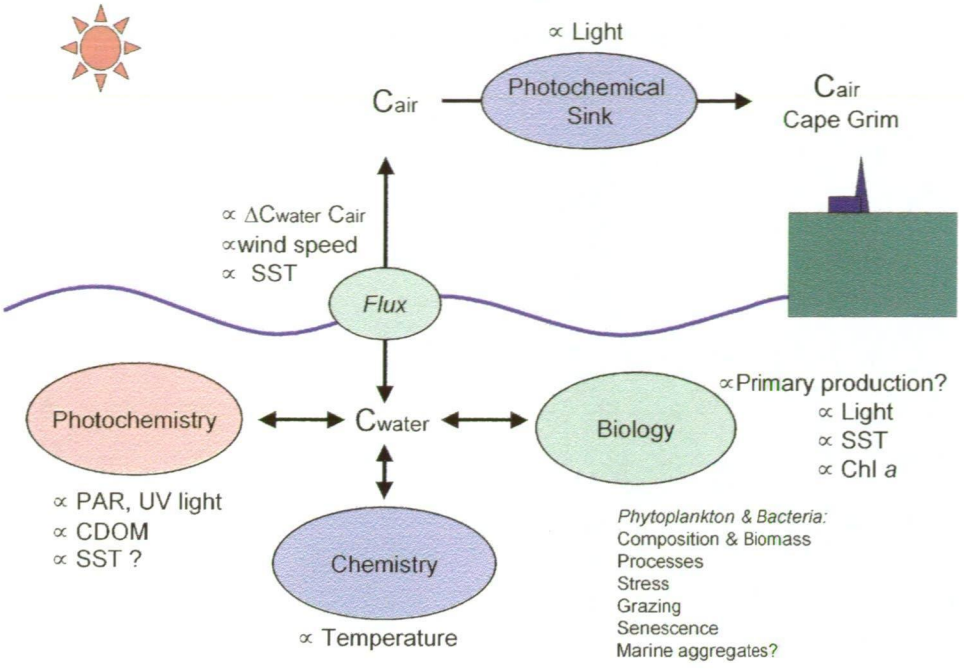

Figure 2.17 Box model of source, sink and rate terms resulting in the concentration of methyl iodide in baseline air detected at a coastal monitoring station (adapted from Hughes *et al.* 2007)

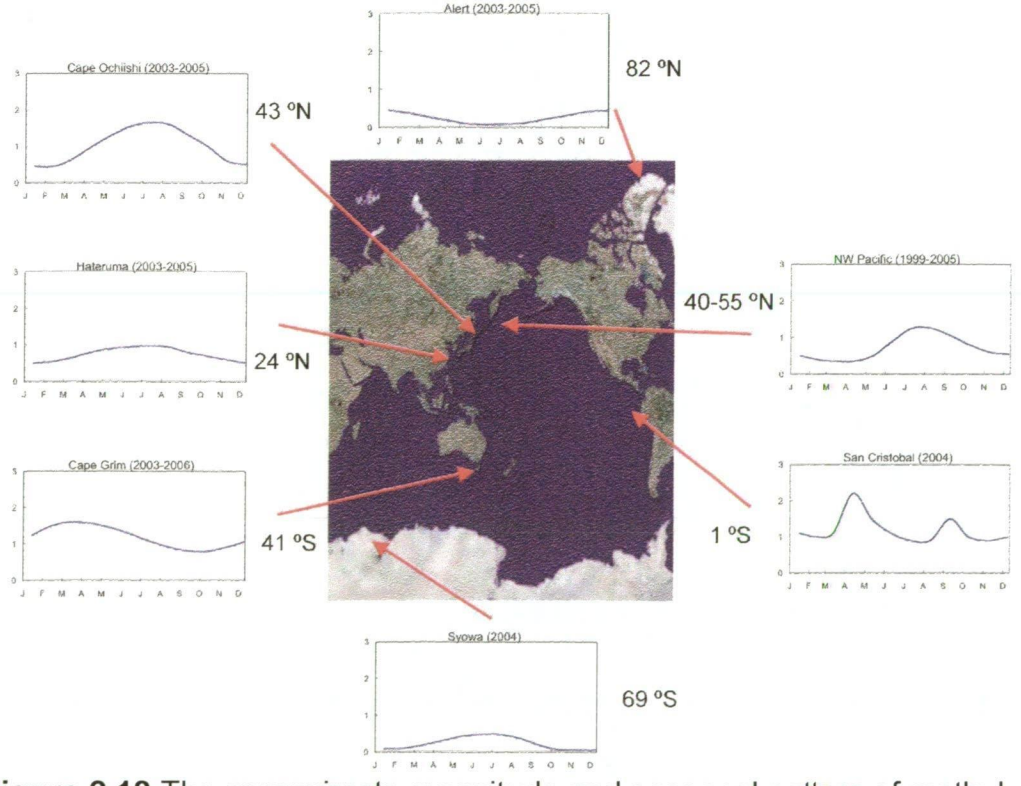

Figure 2.18 The approximate magnitude and seasonal pattern of methyl iodide concentration (in pptv) measured at various air monitoring stations (adapted from Yokouchi *et al.* 2007)

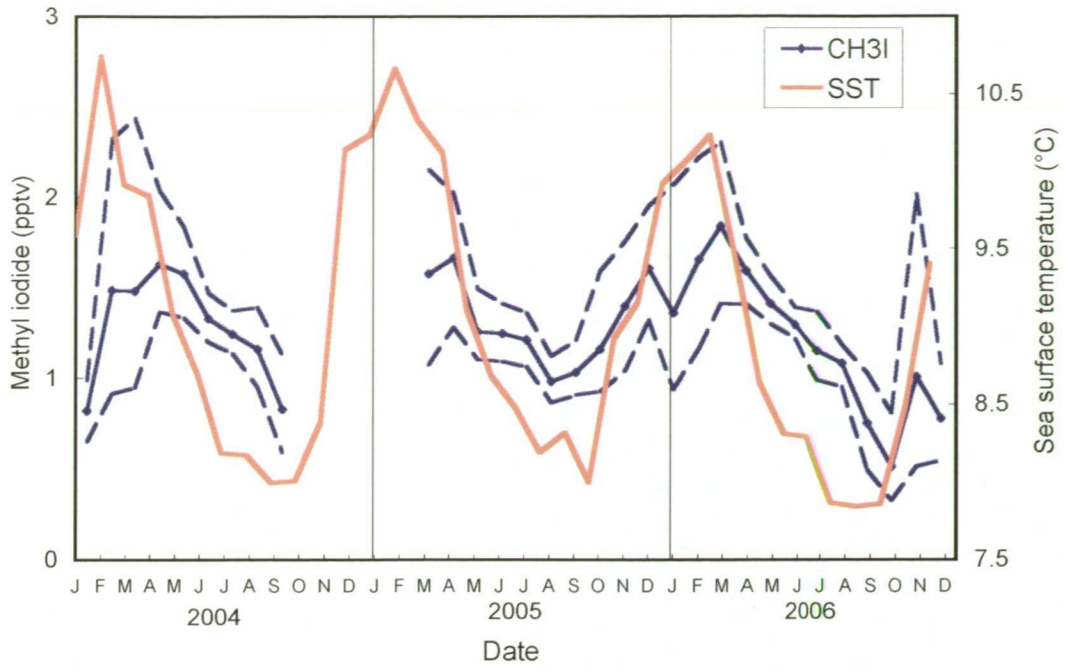

Figure 2.19 Methyl iodide concentration in baseline air at Cape Grim (monthly mean, 90th & 10th percentiles) and monthly mean sea surface temperature of the Southern Ocean (Box 1)

To account for this correlation, Cox *et al.* (2005) has followed the rationale of Yokouchi *et al.* (2001), which attributes the source of methyl iodide entirely to photochemical production. Yokouchi *et al.* (2001) proposed that the photochemical source is dependant on not only solar radiation reaching the sea surface, but also the availability of methyl radicals (after Moore & Zafiriou 1994, Happell & Wallace 1996) and SST through temperature-dependent chemical loss in seawater (after Moore & Groszko 1999). Assuming the ocean and atmosphere are in steady state, this means that the air concentration is dependent on wind speed, SST and seawater concentration of methyl iodide normalized for light intensity. The seawater concentration would be related to the magnitude of the sources of methyl radicals in seawater and to SST in the case that chemical loss is significant in the water. The temperature dependence of the resulting equations is similar to the field data examined by this study. The correlation to DMS at higher temperatures is explained through the connection to organics to act as a source for methyl radicals. See Yokouchi *et al.* (2001) for more details on this theory.

However, as shown in Figure 2.17, and outlined in Chapter 1, there is also a biological source term that must be accounted for. For this reason, the methyl iodide cycle measured at Cape Grim is compared to modeled net primary production of a

large region of the source region in the Southern Ocean (Box 1) in Figure 2.20. Methyl iodide is compared to several ocean variables (SST, PAR, Chl *a*, NPP) in Figure 2.21.

An analysis of the cross-correlation of these seasonal cycles in the continuous section of methyl iodide record from March 2005 to December 2006 (Figure 2.22) reveals the correlation between methyl iodide and SST actually peaked with a month delay (R = 0.78). Peaks in the correlation to Chlorophyll *a* (R = 0.76) and NPP (R = 0.77) occurred with a two-month delay and the peak of correlation to PAR (R = 0.76) occurred with a three-month delay.

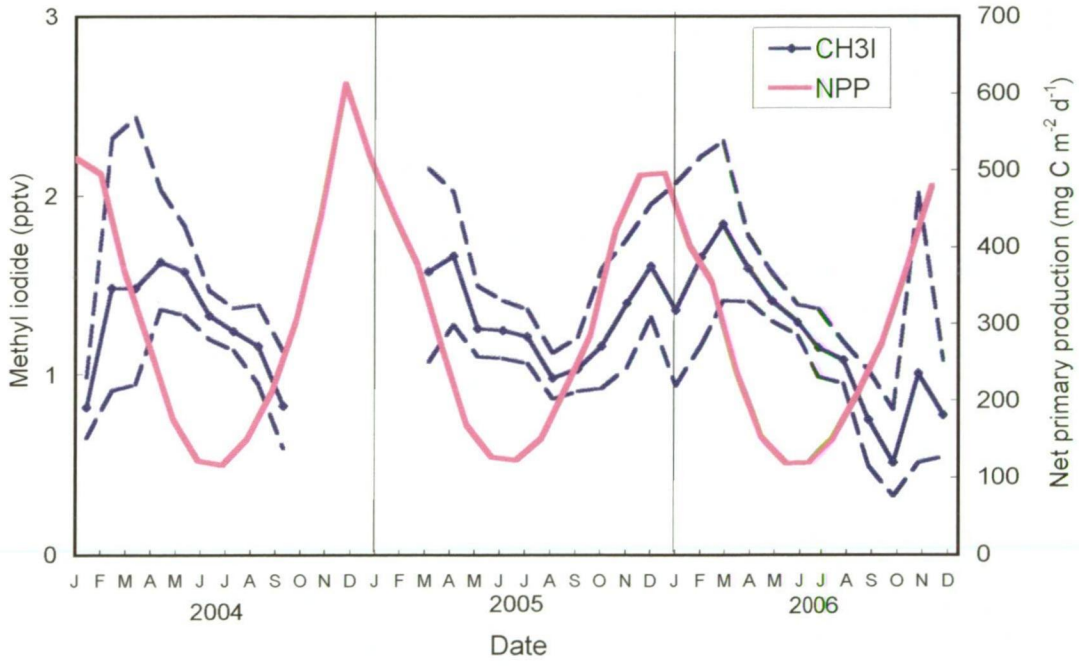

Figure 2.20 Monthly averaged methyl iodide concentration in baseline air at Cape Grim showing 10th and 90th percentile and net primary production (NPP) in surface waters of the Southern Ocean (Box 1)

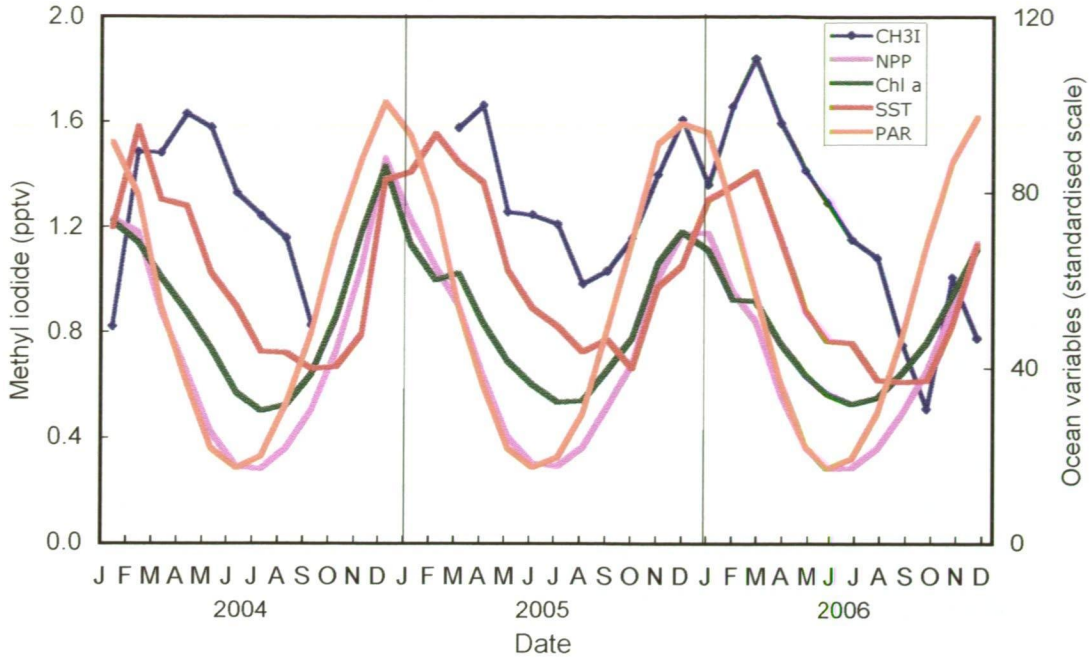

Figure 2.21 Monthly averaged methyl iodide concentration in baseline air at Cape Grim showing 10th and 90th percentile, and SST, Chlorophyll *a*, PAR and NPP in surface waters of the Southern Ocean (Box 1)

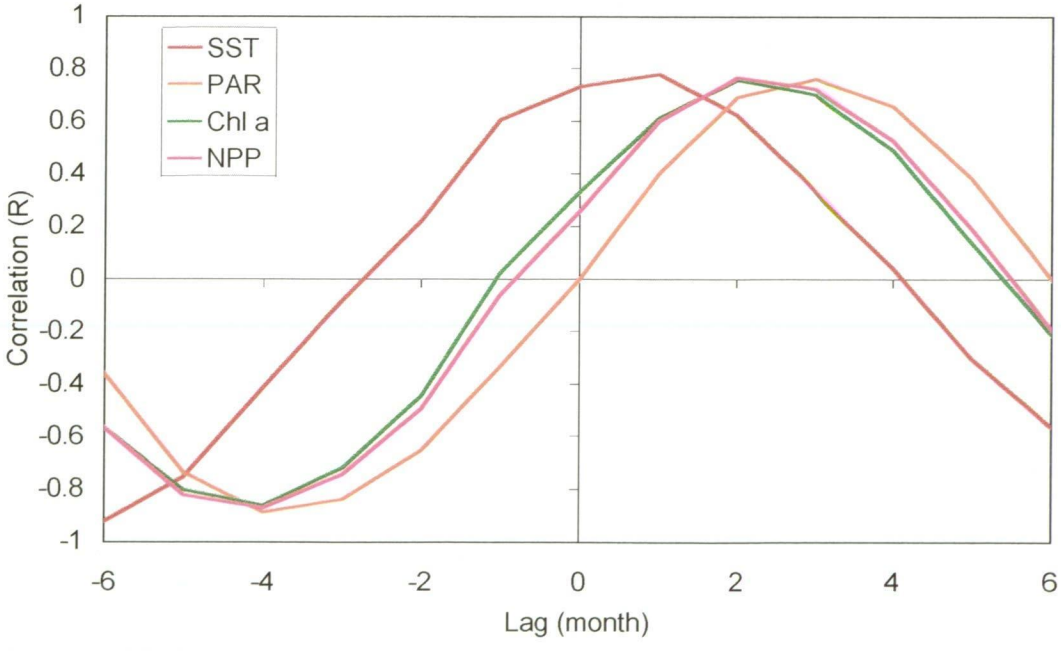

Figure 2.22 Cross-correlation between methyl iodide concentration in baseline air at Cape Grim and SST, PAR, Chlorophyll *a* and NPP in surface waters of the Southern Ocean (Box 1)

Biological production of methyl iodide in the open ocean certainly occurs, and this appears to be detectable at some air monitoring stations. Yokouchi *et al.* (2007) noted that the high concentration of methyl iodide measured at San Cristobal in 2004 might be related to the high biological productivity in the eastern Pacific (Figure 2.18). From the data presented here and the correlations outlined above, the seasonal cycle is consistent with input from both biological and photochemical sources.

In relation to photochemical production of methyl iodide, the lag time of three months between light and the methyl iodide concentration might be explained through the temperature dependence of these processes (after Yokouchi *et al.* 2001). Similarly, in relation to biological production of methyl iodide, the lag time of two months between NPP to the peak of methyl iodide in the atmosphere may be accounted for by the temperature dependence of the processes and also the photolytic sink may suppress the peak in methyl iodide during the period of high light.

There may also exist a natural delay between the peak in productivity and emission of methyl iodide to the atmosphere. This is indicated through culture studies, where some phytoplankton species are shown to produce more methyl iodide after the peak in productivity or biomass, during senescence or even after cell death (Tokarczyk & Moore 1994, Tait & Moore 1995, Scarratt & Moore 1998, Saemundsdottir & Matrai 1998, Smythe-Wright *et al.* 2006).

2.4.3 Daily cycle

The methyl iodide anomaly from the monthly mean plotted against the hour of the day is depicted in Figure 2.23. Methyl iodide concentration showed a clear daily cycle, with higher concentrations in the mornings and lower concentrations in the afternoon. To examine the timing of elevated emissions of methyl iodide, hours when the concentration was >0.8 pptv above monthly mean were isolated. This threshold was determined through qualitative examination of the data. This isolated 54 hourly measurements over 26 events. Interestingly, only two of these events coincided with peaks in methyl bromide concentration throughout the fifteen months of concurrent records. These high events did not occur at a consistent time of day (Figure 2.24). A possible error in daily cycle of this type is from the temperature response of the instrument (an instrumental artefact), this error is not assessed here.

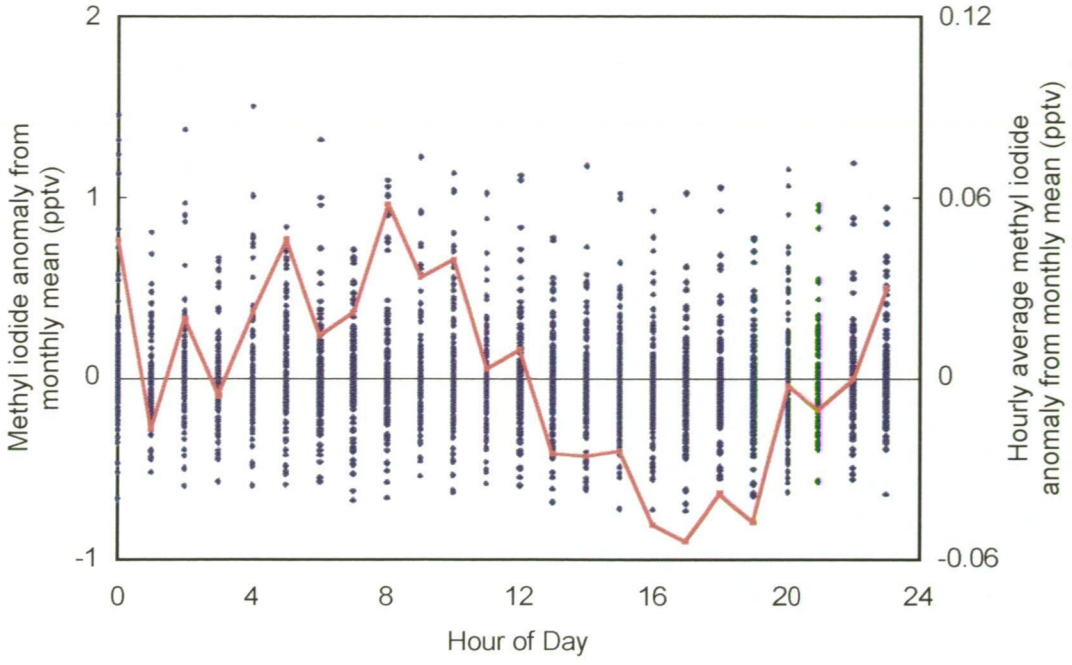

Figure 2.23 Methyl iodide concentration in baseline air at Cape Grim: anomaly from monthly mean plotted against hour of the day, and hourly mean of the anomalies

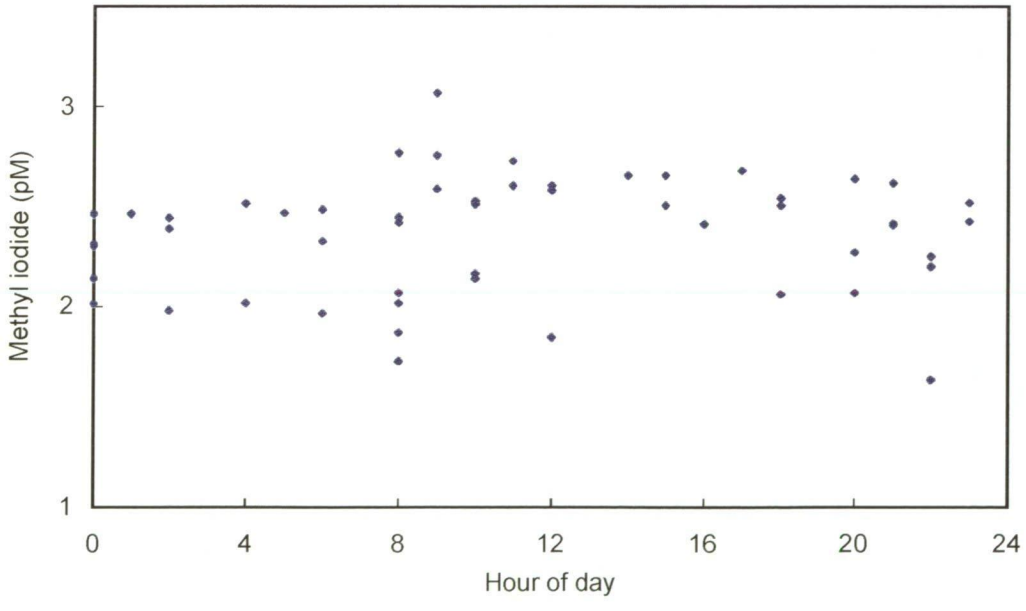

Figure 2.24 Methyl iodide concentrations in baseline air at Cape Grim in events >0.8 pptv above monthly mean plotted against hour of the day

2.4.4 Coastal emissions

To examine any link to coastal phytoplankton biomass, the timing and magnitude of the periods of elevated methyl iodide concentration were compared to coastal Chlorophyll *a* concentration measured from MODIS satellite and modeled net primary production for the coastal waters from Box 2 (Figure 2.25). This comparison shows a trend of elevated methyl iodide events 1 to 2 months following periods of elevated productivity in December to March, but this trend is not entirely consistent. Since biological methyl halide production is not expected to be proportional to primary production due to the complexities in the biological source outlined above, this lack of a correlation is not inconsistent with some source from phytoplankton.

To identify any source from tidally exposed kelp beds the timing and magnitude of the 26 events of elevated methyl iodide concentration were also plotted in comparison to tidal height immediately in front of the station. A typical plot is shown in Figure 2.26, with two elevated incidents on consecutive days (23 and 24 of November 2006), showing no clear relationship to tidal height. Also, the events were not consistent with exposure to sunlight that causes photo-oxidative stress, as events occurred at anytime during the day or night and at any tidal height.

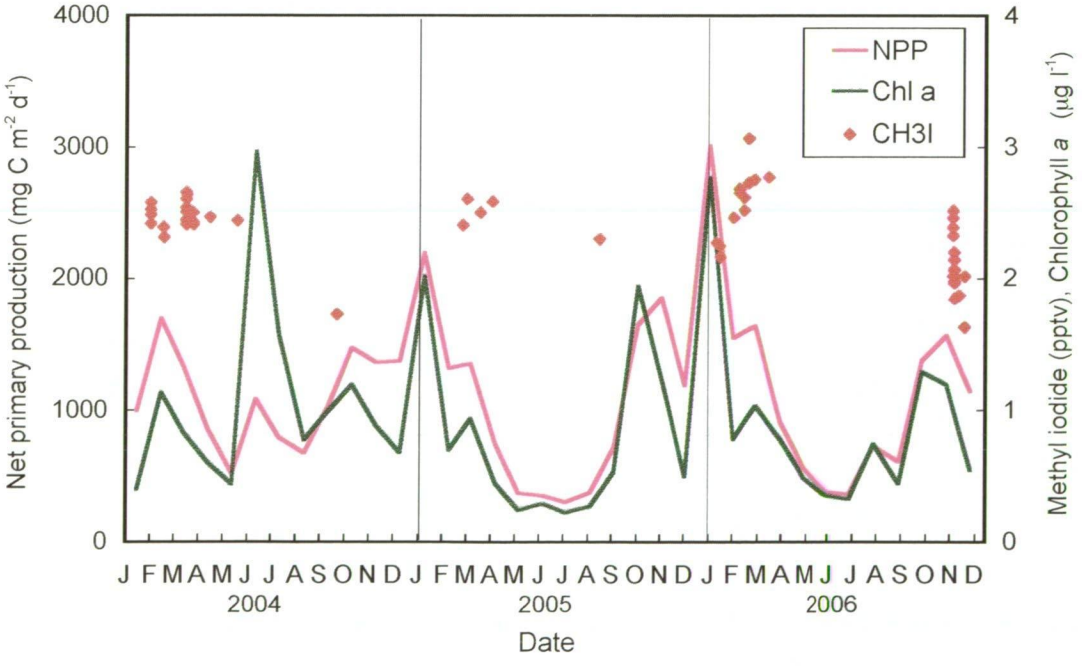

Figure 2.25 Methyl iodide concentration in baseline air at Cape Grim during events >0.8 pptv above monthly mean, and Chlorophyll *a* and modeled NPP in coastal waters of northwest Tasmania (Box 2)

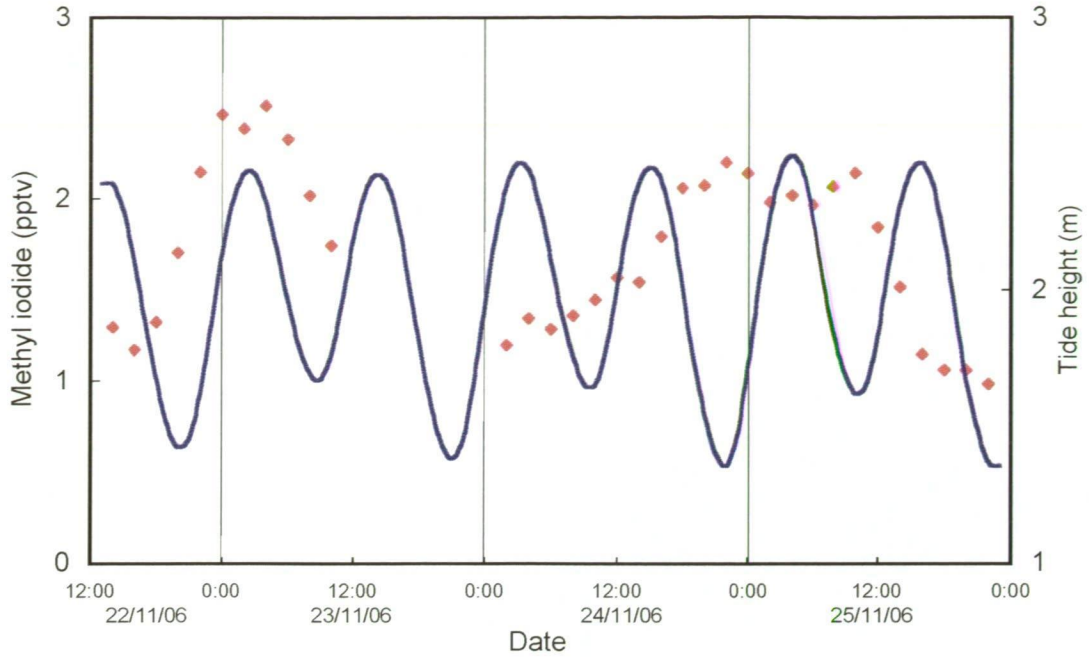

Figure 2.26 Methyl iodide concentration in baseline air measured at Cape Grim on 22-25 November 2006 and tidal height predicted for Cape Grim

2.5 New particles

2.5.1 Annual cycle

Data presented here is also from 1 January 2004 to 31 December 2006 using hourly mean data (26,304 hours). Measurements on the particle instrument are made at less than hourly intervals, and values are averaged for each hour. There are two large breaks in the record between 16/1/2004 and 8/6/2004 (3,457 hours) and between 22/5/2006 and 16/11/2006 (4,202 hours), as well as several small breaks in the record of one or both instruments for maintenance, calibration and repair reducing the data to 18,020 hours. The baseline filter reduced the number of data points to 6,765. Baseline measurements showed an annual cycle (Figure 2.27). There was some inter-annual variability, however analysis of this is limited due to the missing data. The annual cycle was not adequately described by a sinusoidal curve. Monthly averages and standard deviations shown on a common year axis (Figure 2.28) show a bimodal distribution in the monthly averages, with particularly high and variable concentrations are present in October (88 ± 93 cm^{-3}), and with a smaller peak in January (59 ± 82 cm^{-3}). The minimum monthly mean was in June (22 ± 26 cm^{-3}).

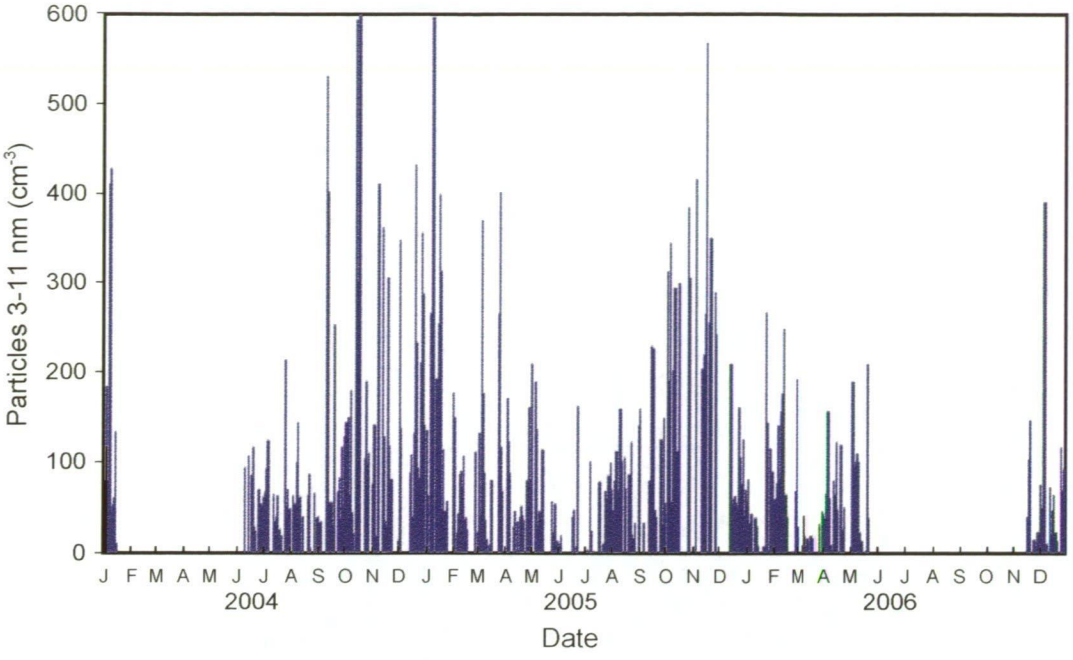

Figure 2.27 Particle concentration 3-11 nm measured in baseline air at Cape Grim 2004-2006

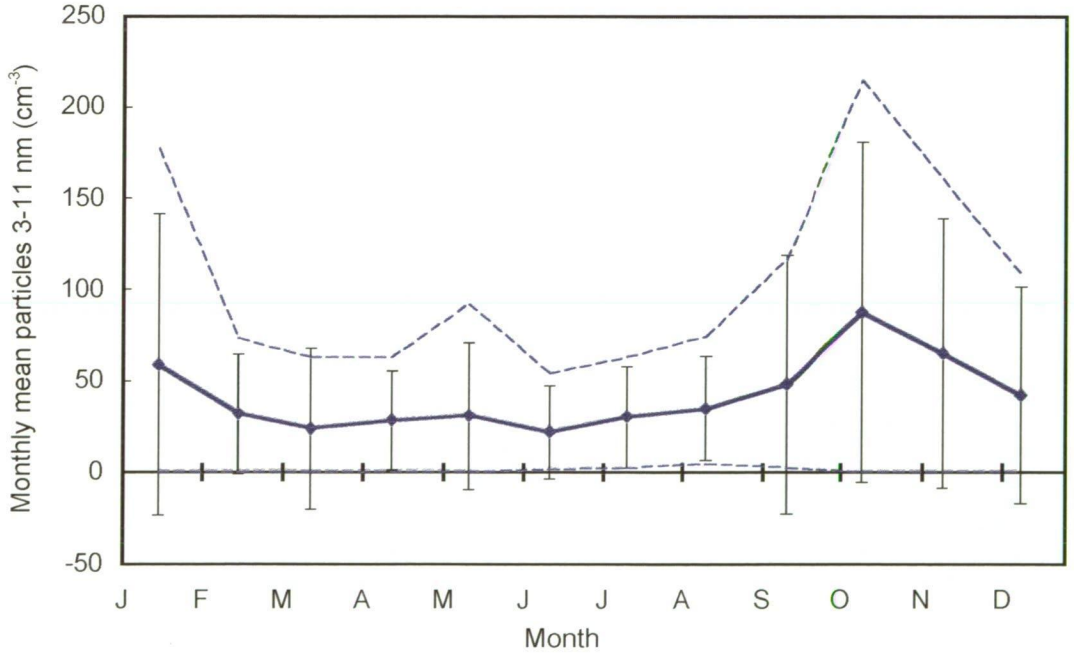

Figure 2.28 Monthly mean particle concentration 3-11 nm measured at Cape Grim from 2004-2006 on a common year axis, showing standard deviations (bars) and 10th and 90th percentiles (dashed lines)

There was not only the highest mean particle number in October, but also the greatest variability, shown in the standard deviations of the monthly means and number of very high peaks. Events of elevated hourly average particle concentration >200 cm^{-3} above the monthly mean were isolated. Again, this threshold was determined by qualitative examination of the data. This isolates 88 hourly measurements over 30 days representing 26 events, and the measurements in each event are plotted against month of the year (Figure 2.29). Elevated events only occurred between September and March, with none in the other months.

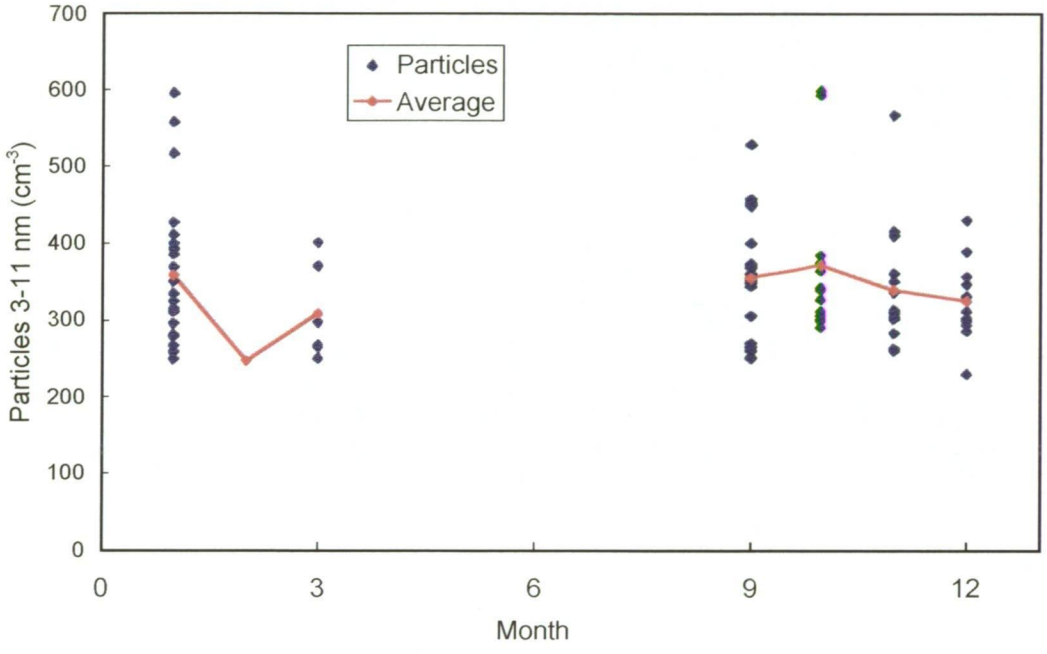

Figure 2.29 Particle concentration 3-11 nm in baseline air at Cape Grim during events >200 cm^{-3} above the monthly mean plotted against month of measurement, and monthly mean in those events

2.5.2 Daily Cycle

Particle count anomaly from the monthly mean is plotted against the hour of measurement (Figure 2.30). The highest anomalies were found in the afternoon and evening, shown both as the highest extremes and a higher mean. A similar distribution is found in the measurements of elevated particle number >200 cm^{-3} above monthly mean, shown in Figure 2.31. There were more elevated events later in the day, and the highest counts were also found in this time.

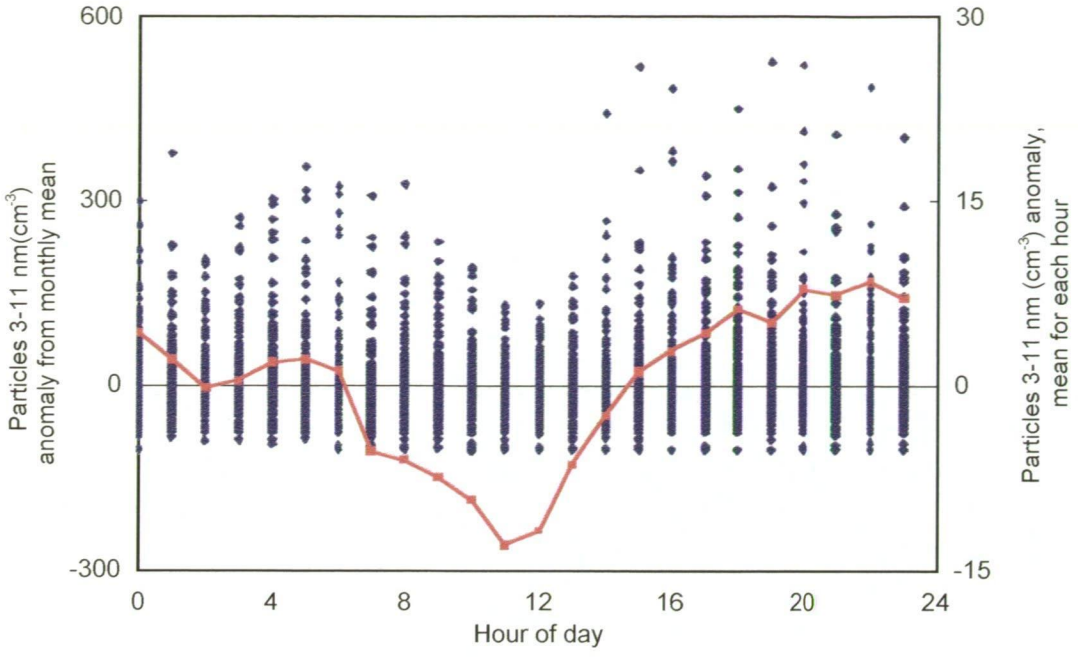

Figure 2.30 Measured anomaly of particles 3-11 nm from the monthly mean in baseline air at Cape Grim in 2004-2006 plotted by hour of day

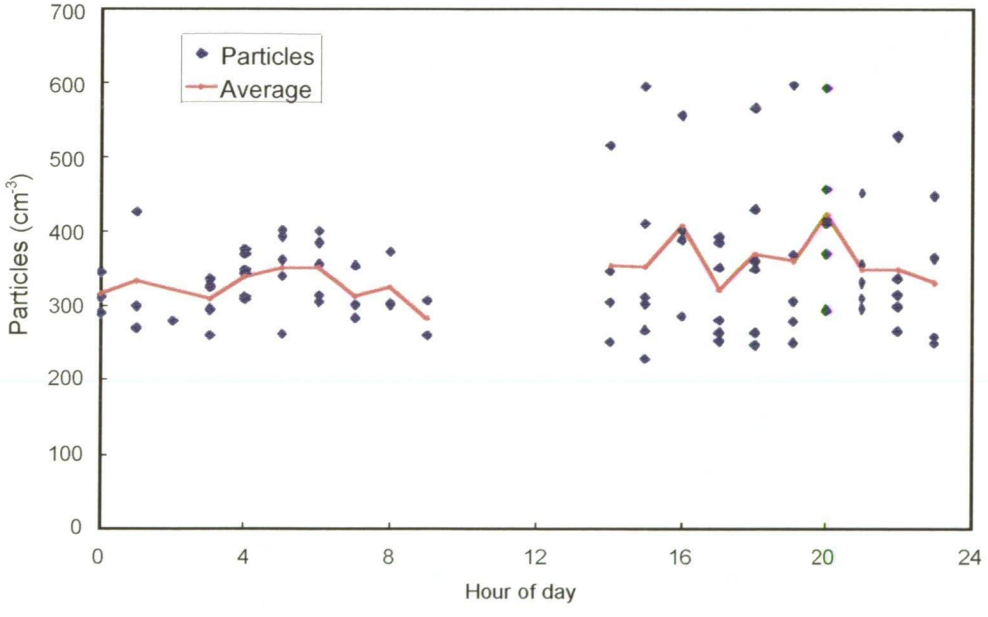

Figure 2.31 Particles 3-11 nm in baseline air at Cape Grim >200 cm^{-3} above monthly mean in 2004-2006, plotted by hour of day

2.5.3 Coastal events

Measurements of elevated particle concentration > 200 cm^{-3} above the monthly mean were examined (88 hourly measurements on 30 days, representing 25 events, as

mentioned above) and compared to the tidal cycle. Of these 25 events, 19 showed a peak that started in the afternoon, 5 showed a peak that started in the morning and there was one event of three consecutive peaks.

Of the morning events, three events showed a correlation to low tide and two did not, and generally peaked between 4 and 6 am AEST (no daylight savings). The morning events had a lower peak particle number than the afternoon events. Of the afternoon events, four events showed no correlation to low tide (Figure 2.32), and eight did (Figure 2.33) and seven events were ambiguous. Whether the event showed a correlation to tide or not, the peak in particle numbers was between 2 and 9 pm, and most commonly at 6 pm or 8 pm. One unusual event occurred on the 16-17 January 2005, whereby three consecutive peaks in particle number were positively correlated with high tide (Figure 2.34).

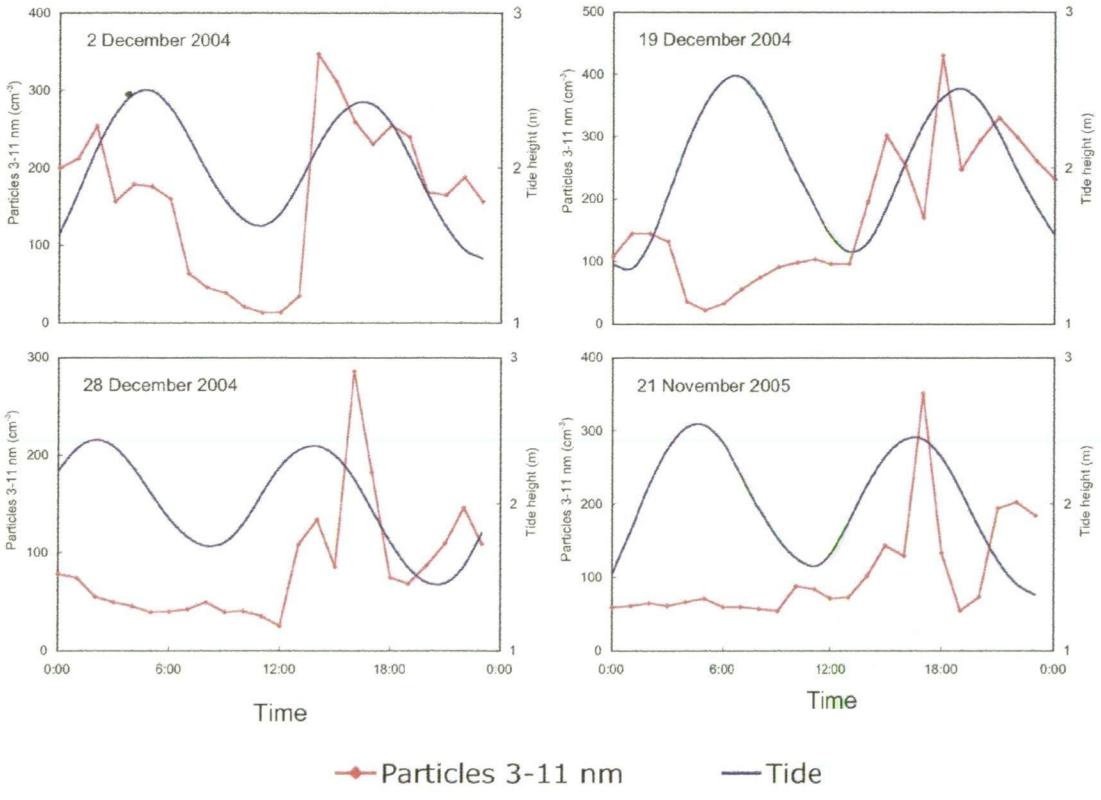

Figure 2.32 Hourly mean particle concentration 3-11 nm measured in baseline air at Cape Grim and estimated tide height at Cape Grim, displaying incidences of elevated particle number >200 above monthly mean not beginning at or near low tide

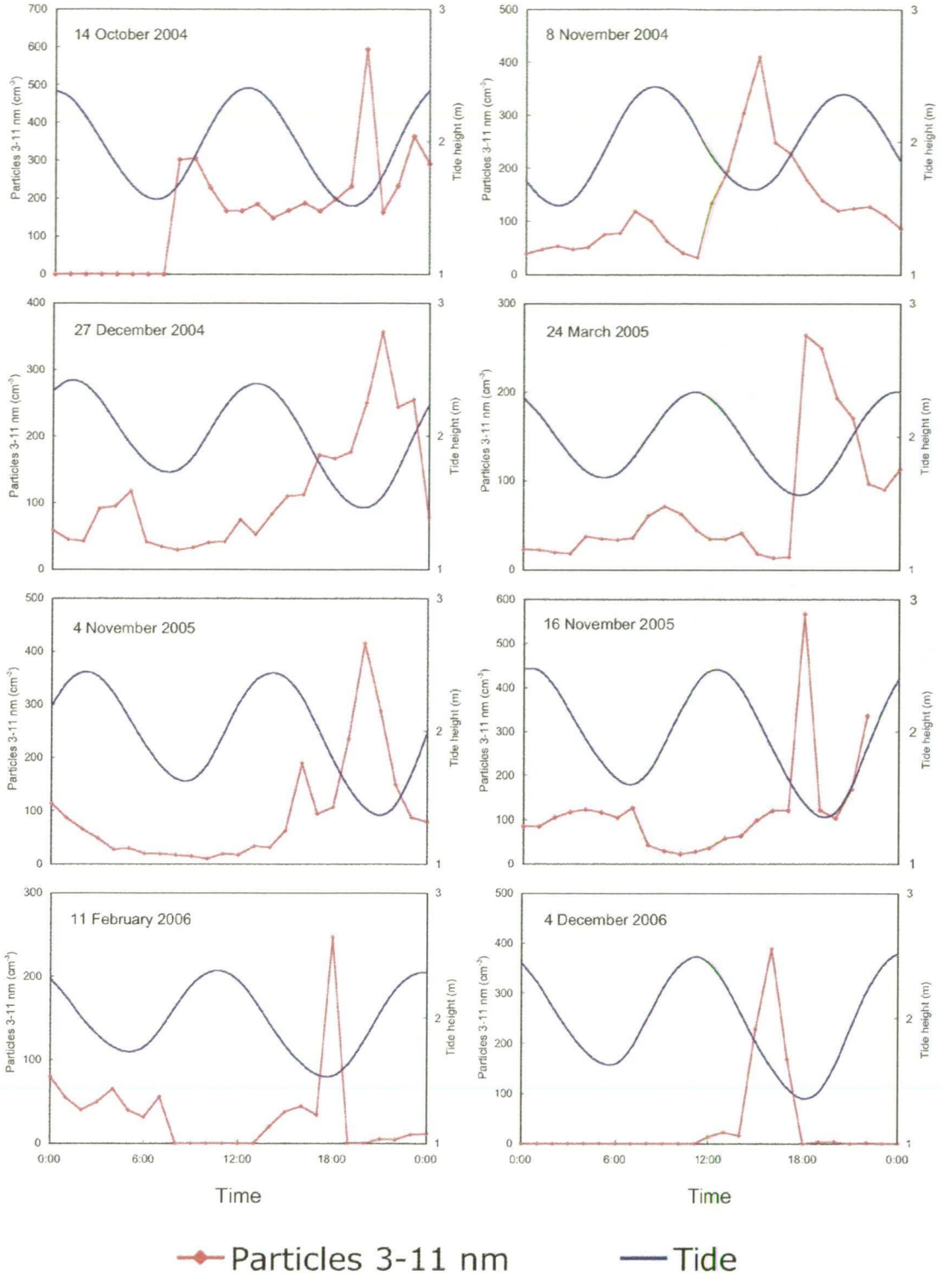

Figure 2.33 Hourly mean particle concentration 3-11 nm measured in baseline air at Cape Grim and estimated tide height at Cape Grim, displaying incidences of elevated particle number >200 above monthly mean beginning at or near low tide

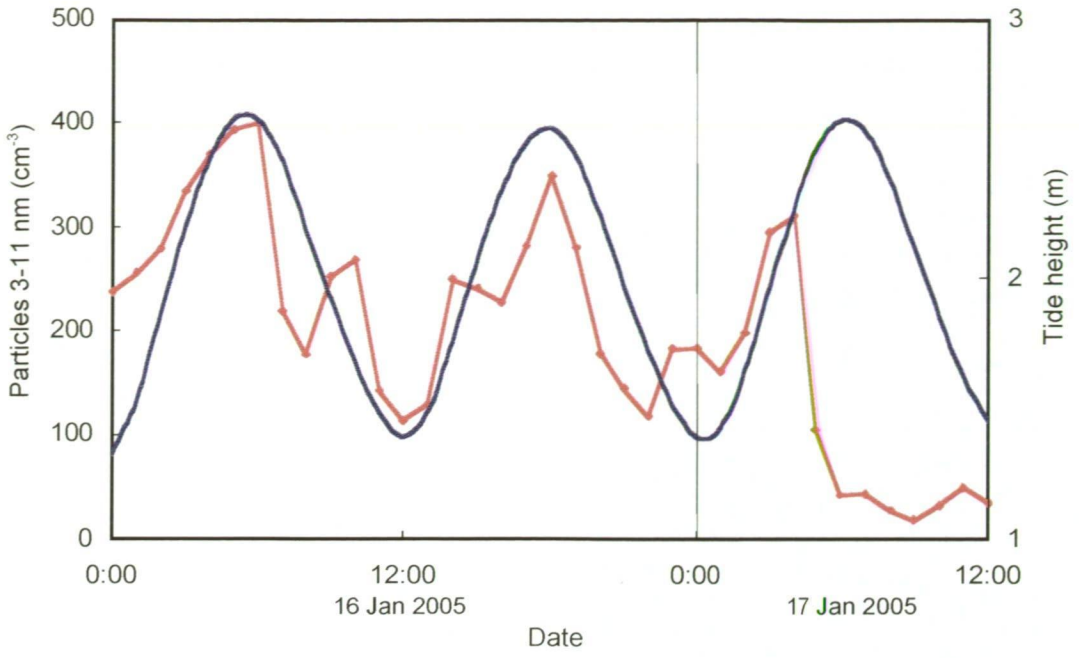

Figure 2.34 Hourly mean particle concentration 3-11 nm measured in baseline air at Cape Grim and estimated tide height at Cape Grim 16-17 January 2005, showing three consecutive peaks in particle number partially correlated with tidal height

2.6 Discussion & Conclusions

These records give context to the ocean measurements in the subsequent chapters. Baseline air at Cape Grim is of an entirely marine origin, and the major source and sink for the methyl halides in this air is the ocean. Therefore, the time series of methyl halide concentration measured at the Cape Grim station during baseline conditions will give an indication of the net source and sink of the ocean upwind of the station. For Cape Grim this is a large area of the Southern Ocean south of Australia. This is especially true for methyl iodide, which has a lifetime of only a few days, compared to the longer-lived methyl bromide.

Identifying baseline air depends upon effective filtering of the data. The baseline filter applied here uses the established convention of wind direction and radon concentration, but with some novel modifications. These changes to the wind sector and using the radon threshold on all data seem to yield reliable quality data. The events of elevated concentration appear to be consistent with the coastal processes in question, rather than pollution events from non-baseline air. Also, if the filter was

insufficiently strict, then the average concentrations would show an increase compared to the previous year's data, which is not the case.

2.6.1 Methyl bromide

The average concentration of methyl bromide in the boundary layer is 9 to 10 pptv, with an inter-hemispheric ratio of 1.2 to 1.4 with higher concentrations in the northern hemisphere (Orlando 2003). Average concentration in baseline air at Cape Grim was previously measured to be 8.05 pptv (Cox *et al.* 2005), using the previous GC-MS-ADS instrument. The concentration in baseline air at Cape Grim represents very clean marine air, so is expected to have a lower concentration than the global average. The average concentration in baseline air in this analysis is 7.28 ± 0.15 pptv, which is lower than the previous study. The global average concentration of methyl bromide in the troposphere is falling since the ban through the Montreal Protocol, which may explain this difference. However, since the data has not been through the formal AGAGE validation process, some of this apparent reduction may be due to imperfect calibration. For this reason, the temporal trends within the dataset are the focus of this analysis rather than the absolute values. It is also possible that these differences may be at least partially due to instrumental differences as well as calibration issues.

Previous measurements show a seasonal cycle of methyl bromide concentration in the northern hemisphere, but not in the southern hemisphere (Wingenter *et al.* 1998, Simmonds *et al.* 2004), resulting in a seasonal cycle in the inter-hemispheric concentration ratio. Northern hemispheric variation is approximately 1.3 pptv (12.9% peak-trough) at Mace Head (Simmonds *et al.* 2004), and of a similar magnitude in Alaska (14% peak-trough, Wingenter *et al.* 1998) and Alert (Yokouchi *et al.* 2000). This seasonality in the northern hemisphere indicates that the atmospheric sink may be dominated by the hydroxyl radical in this region (Simmonds *et al.* 2004).

A seasonal cycle was not previously observed in baseline air at Cape Grim (Simmonds *et al.* 2004, Cox *et al.* 2005). The lack of a strong and simple seasonal cycle was attributed by Simmonds *et al.* (2004) to a complex interaction of out-of-phase atmospheric and oceanic sinks. However, modeling work suggests that very small seasonal changes should be present (Reeves 2003). Using this recent data and

this filtering technique, there is evidence of some small, non-sinusoidal seasonal changes. This appears to be consistent with the modeling work. Also the lack of a smooth sinusoidal cycle is consistent with the assertion by Simmonds *et al.* (2004) of the complexity and phase of the sources and sinks. Further data are required to confirm this is a recurring annual cycle rather than an anomalous pattern, or influenced by a long-term trend.

There was a lack of a daily cycle in methyl bromide concentration indicating a lack of rapid photolysis in sunlight over the day. The lifetime of methyl bromide in the troposphere is approximately 0.7 years (Orlando 2003), so this finding is consistent with this lifetime.

2.6.2 Methyl iodide

Atmospheric concentrations of methyl iodide in the boundary layer were typically within 0.1 to 5 pptv, with greater concentrations in the tropics compared to higher latitudes (Yokouchi *et al.* 1997). The average global mixing ratio is between 1 and 3 pptv (Orlando 2003). These measurements in baseline air at Cape Grim fall at the lower end of this previously measured range (0.87 to 1.62 pptv).

Previous measurements at tropical sites showed no strong seasonal cycle whereas mid-latitude measurements showed a seasonal cycle with a maximum in summer to autumn and high-latitude sites showed a seasonal cycle with higher values in winter (Yokouchi *et al.* 2007, Figure 2.19). Previous measurements at Cape Grim indicated methyl iodide concentration had a distinct sinusoidal seasonal cycle with highest concentration in early autumn of 1.62 pptv and lowest in spring of 1.3 pptv (Cox *et al.* 2005). The presence and timing of this cycle is confirmed in these measurements. The seasonal maximum was also the same as the previous data, 1.62 pptv, but there was a lower minimum of 0.87 pptv and correspondingly larger amplitude. This difference may be due in part to the difference in filtering technique, but may reflect a change in the marine source, sink and flux terms represented in the measurements.

The seasonal cycle was well correlated to sea surface temperature in the oceanic source region. This is consistent with photochemical production with a temperature dependence as found previously (Yokouchi *et al.* 2001) but also from biological

sources with a similar temperature dependence with a possible influence of a natural lag time as well as the photolytic sink.

Methyl iodide measurements showed a daily variation with lower concentrations in the afternoon. The atmospheric lifetime of methyl iodide in the troposphere is only 3 to 5 days due to rapid photolysis (Bell *et al.* 2002, Roehl *et al.* 1997), so the daily cycle is consistent with this. High concentration events were sporadically but imperfectly correlated with periods of high biological productivity in coastal waters up to 10 km offshore.

2.6.3 Coastal emissions of methyl halides

High biological production of methyl halides at the coast, especially by macroalgae, may be detected in measurements at atmospheric monitoring stations. For example, strong coastal emissions of halocarbons have been found in measurements at an air monitoring station at the coast of New Hampshire, USA (Zhou *et al.* 2005). Halocarbon release from macroalgae can be initiated by photo-oxidative stress (Pedersen *et al.* 1996), which is initiated when the kelp is exposed to the air and high light. Therefore, halocarbon measurements at a coastal station may also show correlations to low tide. High coastal emissions of polyhalomethanes (CH_2ICl, CH_2IBr, $CHBr_3$, CH_2I_2) have been detected at the Mace Head station and are correlated with low tide during light winds that pass over kelp beds (Carpenter *et al.* 1999). This was clearly seen in the concentration of CH_2I_2, $CHBr_3$ and IO_3 during a special campaign at Mace Head (Carpenter *et al.* 2000, O'Dowd *et al.* 2002a). The strongest emission of the polyhalomethanes associated with low tide at Mace Head was when low tide occured between late afternoon and early morning when there is low light (Carpenter *et al.* 1999). At Mace Head, emission of I_2 from coastal beds of macroalgae was also initiated by photo-oxidative stress, which occurs during periods of low tide and full sun (Saiz-Lopez *et al.* 2004).

At Mace Head, elevated concentrations of methyl iodide were not detected at low tide. This has not previously been examined at Cape Grim. There are factors that suggest that detecting such peaks are more likely at Cape Grim compared to Mace Head and other factors that suggest it may be less likely. Firstly, methyl iodide concentrations are higher at Cape Grim than at Mace Head. Also, the alkyl halides

CH_2I_2, CH_2IBr & CH_2ClI were found to be below detection limits of 4 pptv at Cape Grim station, unlike Mace Head (Carpenter *et al.* 2003). Therefore, methyl iodide is a relatively more important component of the total iodine concentration at Cape Grim compared to Mace Head (Carpenter *et al.* 2003). However, Cape Grim station is situated on top of a cliff 94 m above sea level and the kelp beds do not extend far off shore. This presents a major barrier to measuring emissions of trace gases from kelp beds at the bottom of the cliff. Mace Head station is virtually at sea level, and has been noted that emissions from kelp are more likely to be detected there (Carpenter *et al.* 2003).

In these measurements, both methyl bromide and methyl iodide lacked any clear relationship to tidal cycle in front of the station, both in the mean and events of elevated concentration. The emission of methyl halides at the coast can be highly localized, so detection on top of the cliff may be impossible. Therefore, there may be high emissions of methyl halides from the kelp at the coast that is not detected at the station. This is investigated further in Chapter 5.

2.6.4 New Particles

New particles as indicated by the difference between the 3 nm and 11 nm size range (after Jimi *et al.* 2003) in strictly filtered marine air showed an hourly mean between 0 and 600 cm^{-3}, which was much lower than in polluted air. The particle number showed a seasonal cycle in both average number and variability, with a maximum in October and a smaller maximum in January. The measurements showed a distinct daily cycle, with higher measurements in the early morning and in the late afternoon. High peaks >200 cm^{-3} above the monthly mean occurred only at these times, some of which occurred correlated to low tide and others did not.

From the data presented here, it appears that there are rare events of elevated particle numbers originating from the coast, and these are detectable at the station. The number and magnitude of coastal particle emission appears much less than at Mace Head. There were only 25 events over 3 years at Cape Grim, compared to 58% of all days at Mace Head (Yoon *et al.* 2006). The hourly mean particle number in these events was 264 to 593 cm^{-3} in the 3-11 nm range and 529 to 2072 cm^{-3} in the > 3nm size, which is relatively modest.

The regular and predictable coastal bursts of particles detected at the Mace Head station correlated with low tide and full sun (Yoon *et al.* 2006) are linked to emission of iodine (I_2) from coastal beds of macro algae (Saiz-Lopez *et al.* 2004). The particles formed are composed of iodine oxides (O'Dowd *et al.* 2002b). This may not be the case at Cape Grim, these modest particle emissions may be from another source, either from the kelp or elsewhere. The event on 11th February 2006 coincides with measurements made at the beach, and will be discussed further in Chapter 6.

Chapter 3. Production of methyl halide in the open Southern Ocean west of Tasmania

3.1 Introduction

Methyl halide concentrations in surface seawater of the open ocean are variable in space and time throughout the world's oceans. Areas of open ocean can variously represent a source or sink of methyl halides, dependent on the saturation anomaly.

Measurements of methyl halide concentration and saturation were made in the open ocean south of Australia, within the upwind fetch zone of the Cape Grim station. The methyl halide concentration and saturation in these waters were compared with other regions of ocean, and any regional differences were identified. Several specific aspects of the marine source were examined closely including the suitability of the relationship between methyl bromide saturation and sea surface temperature (SST) made by King *et al.* (2002) for this region. Also, the relationship of methyl halide concentration to distance from the coast was examined, as was the correlation between biological variables and methyl halide concentration to find evidence of a biological source. Since an analytical instrument suitable for taking to sea was not available, a novel method of was tested and used in this study.

3.2 Methods

3.2.1 Cruise track

Samples were taken on board the CSIRO Marine and Atmospheric Research (CMAR) cruise SS0306 on board the RV Southern Surveyor in March 2006 between Hobart and Esperance, Australia. Water samples were taken from Niskin bottles on 8 CTD casts; surface samples were taken from each CTD cast, sub-surface samples were taken on 5 CTD casts, labeled in Figure 3.1. In addition, 26 surface samples

from the underway seawater line were taken opportunistically along the cruise, including a series of 10 samples moving away from the coast of Tasmania and six samples on the approach to Western Australia (Figure 3.1). Concentration of nutrients nitrogen, phosphate and silicate were measured using a Lachat QuickChem 3000 auto-analyzer (using standard QuickChem methods). Photosynthetic pigment concentrations were analysed using a C_8 column and binary gradient High Performance Liquid Chromatography (HPLC) system, following a modified version of Van Heukelem and Thomas (2001) and commercial and international standards (Sigma; DHI, Denmark).

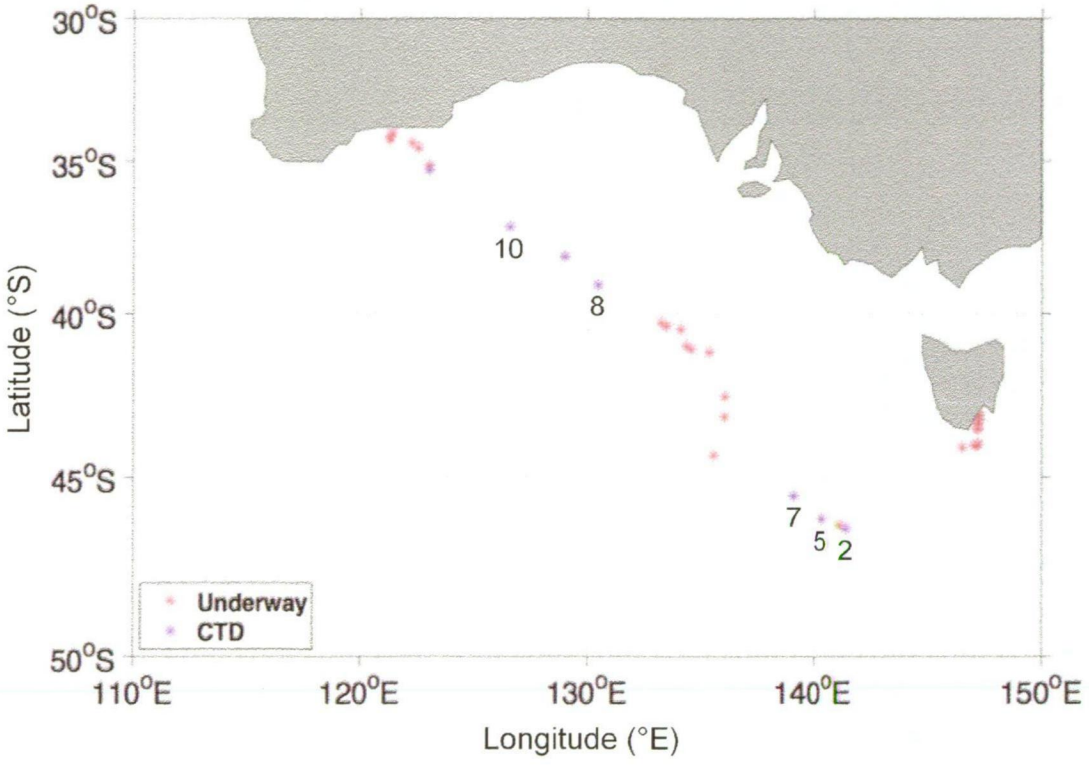

Figure 3.1 Cruise track of Southern Surveyor voyage SS0306 March 2006 showing CTD and underway sampling locations, CTDs where subsurface measurements of methyl halides were made are labeled with CTD number

3.2.2 Methyl halides

For underway sampling, seawater was pumped from the ships intake located at 3 m depth, through a de-bubbler and an in-line fluorometer. Flow rate was approximately 0.8 l min^{-1}. Seawater was continually flowing from underway line into a 500 ml bucket. To sample for methyl halides a 100 ml sample was taken from the base of the

bucket into a glass syringe with three rinses ensuring no air bubbles. Samples were stored at 4 °C in the fridge in the dark until purging and trapping, which was completed within an hour of sampling.

Samples were also taken from the Niskin sample bottles on the CTD. Bottles were sampled from the surface station on each CTD, and from various other depth stations on some casts (see Figure 3.1). Samples were taken using a 100 ml glass syringe directly from the Niskin bottle outlet, with three rinses ensuring no air bubbles remined in the syringe. Again, samples were stored at 4 °C in the dark before purge and trapping was performed within two hours.

Analysis of methyl iodide and methyl bromide was performed using a new method developed for this cruise. The method was a modified version of the purge and cryo-trap gas chromatography with electron-capture detection (GC-ECD) method described in Sturrock *et al.* (2003), after Baker *et al.* (1999, 2001). The method was separated into two parts, with purge and cryo-trapping of samples completed immediately on board ship, trapped samples stored on liquid nitrogen and analysis completed on shore.

Seawater samples were purged within a 50 ml sparge chamber, the air dried with an ice water bath and nafion, then cryo-trapped according to Sturrock *et al.* (2003) onto a 0.16 cm i.d. x 85 cm stainless steel coil trap maintained at –150 °C (Figure 3.2). Each trap was maintained at this temperature while it was disconnected and capped (Swagelok stainless steel 1/8" caps) under a flow of helium to ensure no external air ingress, and plunged immediately into liquid nitrogen (-196 °C) for storage. On shore, coils were transferred to dry ice (-78.5 °C), for air and land transport (a period of one week) and then analyzed, the effect of storage at this lower temperature was not assessed. Total storage time was a maximum of one month.

For the second part of the analysis, each coil was equilibrated at –150 °C, uncapped and connected to GC lines under a flow of helium. After at least 1 minute of flushing with helium, the sample was delivered into the GC by plunging the coil into boiling water and the rest of the GC-ECD procedure was followed Sturrock *et al.* (2003).

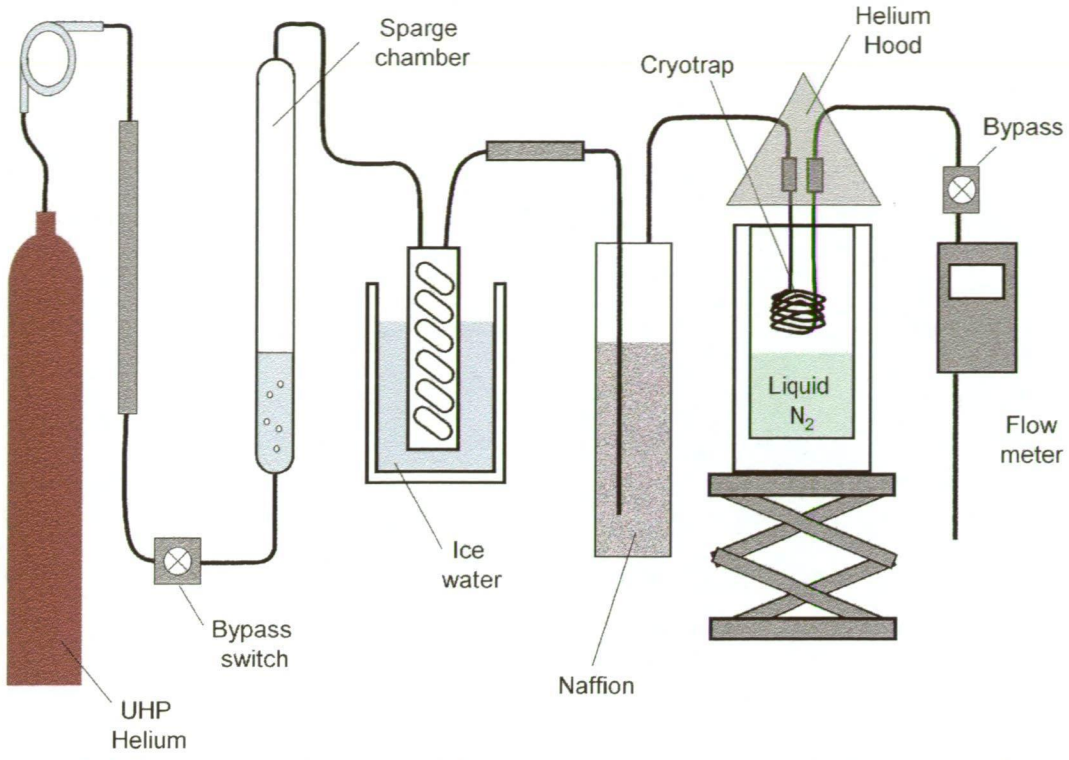

Figure 3.2 Schematic diagram of the purge and cryo-trap apparatus used to extract methyl halides from seawater and trap onto steel coils

3.2.3 Analysis of error in the novel purge and trap method

Errors present in the basic method reported in Sturrock *et al.* (2003) are ±7% for repeats of a seawater sample, and ±16% between seawater samples collected as a pair. Added to this is the additional error caused by storage.

Two experiments were performed prior to the voyage to assess the error resulting from storage. A single water sample was purged and trapped onto multiple steel traps following the standard method (Sturrock *et al.* 2003), then each was capped as described above and stored on liquid nitrogen before analysis at various time steps. The first storage experiment was run using inshore seawater over a short time period (12 hours) and the second was run using inshore seawater from a different location over a longer period (26 days). Each trial consisted of an initial measurement and four time steps. Measured seawater concentrations are shown in Figures 3.3 and 3.4.

Since there was only a single measurement at each time step and no replicates, the estimate of error can't be considered statistically significant. However, it does appear

that the short-term storage caused a drop of 1-2 pM (approximately 5-10%) compared to an immediate analysis, with occasional measurements showing considerable change of up to 40% (6 hour station in methyl bromide). Longer-term storage appeared to consistently result in a similar decrease in concentration of 1-2 pM (10-40%) compared to immediate analysis. These results indicated that the concentrations measured on the cruise were an underestimate of the actual seawater concentration by 10-40%.

A series of standard additions of deuterated methyl iodide (CD_3I) was performed to assess the errors present in storage. Six sets of CD_3I additions were performed, adding two concentrations of CD_3I. Additions were typically 80-160 pM, and then a second addition of 160-330 pM. The concentration of added CD_3I was compared to measured CH_3I+CD_3I. Variation in measured CD_3I concentration from expected was approximately ±8.5%.

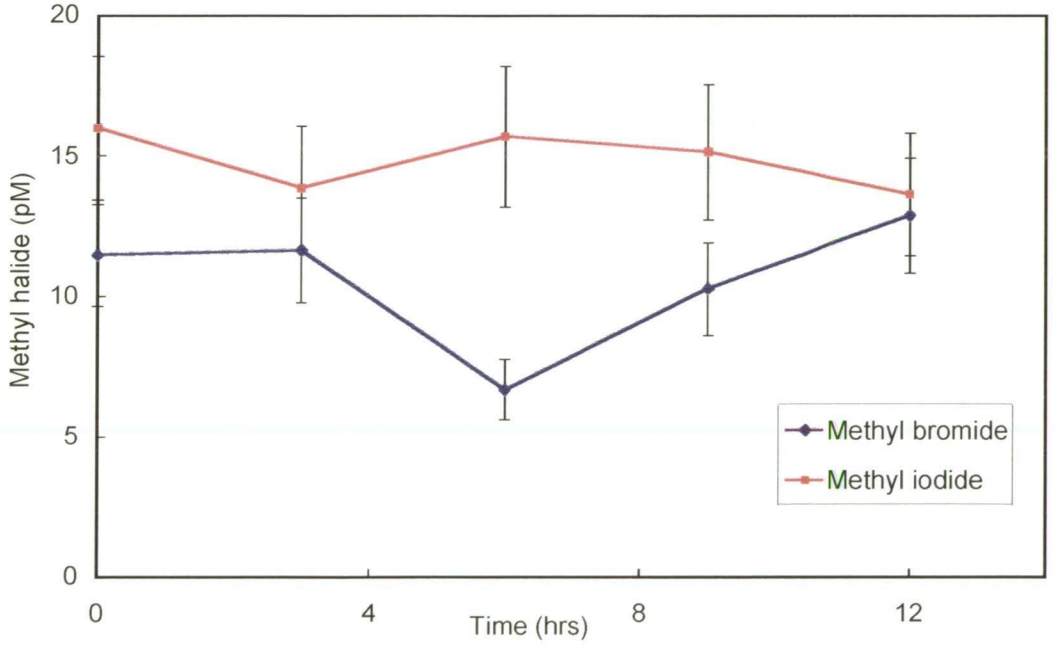

Figure 3.3 Seawater concentrations of methyl halides in short term storage experiment 1 with time steps at 0, 3, 6, 9 & 12 hours (16% error from standard method are shown)

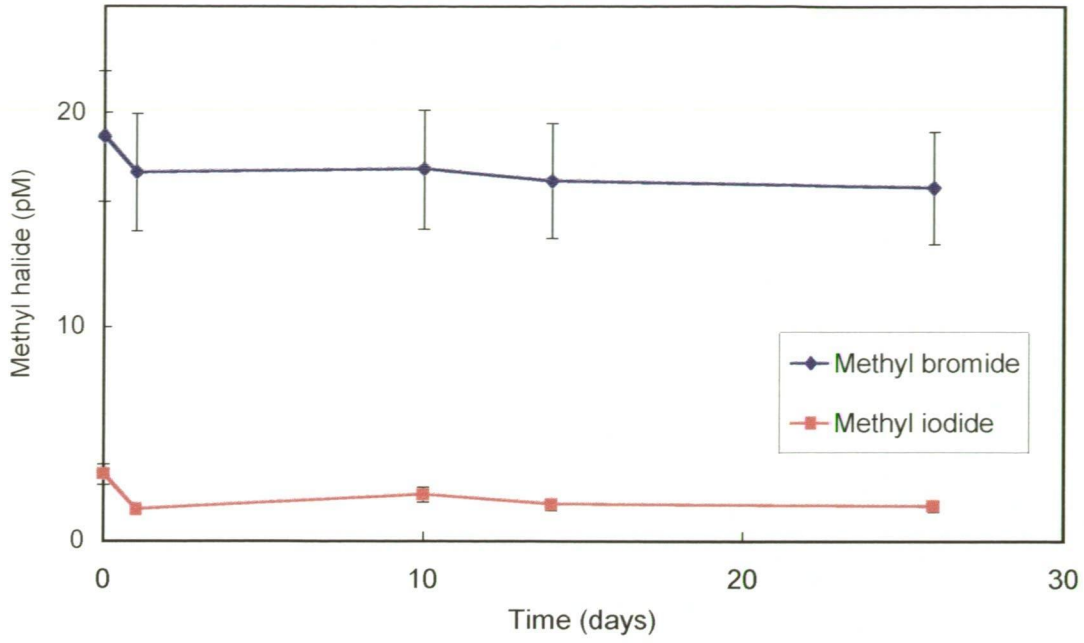

Figure 3.4 Seawater concentrations of methyl halides in long term storage experiment 2 with time steps at 0, 1, 10, 14 & 26 days (16% error from standard method are shown)

3.2.4 Inorganic iodide

Iodide was sampled and measured by CSIRO Marine and Atmospheric Research (CMAR, E. Butler) in conjunction with the Australian Centre for Research on Separation Science (ACROSS, J. Hutchinson) at the University of Tasmania.

Samples were taken from surface Niskin bottles of each CTD and from the underway seawater line at the same time as methyl halide samples. For each sample, a 250 ml polycarbonate bottle was filled directly from the seawater line or Niskin bottle with three rinses. Within 2 hours the sample was filtered with a 0.4 um HA millipore filter and the filtrate retained in a rinsed bottle to obtain a 200 - 250 ml sample. Filtered samples were stored at 4 °C until analysis.

Within twelve months, iodide in seawater was measured using a transient isotachophoresis capillary electrophoresis (tITP-CE) method based on that of Huang *et al.* (2005). A Beckman Coulter P/ACE MDQ capillary electrophoresis instrument was used. This instrument suffers no problems with carryover contamination. The electrolyte system was 0.5 M MES buffer at pH 6.5 and 0.5 M NaCl with 15 mM

CTAC surfactant added to slow the motility of iodide. The uncoated capillary was rinsed at a pressure of 2 bar for 3 minutes, then the sample was injected at 503.3 mbar for 10 seconds. ITP was performed at 200 microamps for 2.5 minutes, and then separated for 60 minutes using 200 microamps.

3.3 Results & Discussion

3.3.1 Oceanography

The area of ocean examined here has a complex circulation consisting of the Leeuwin Current seasonally extending around from the coast of Western Australia as far across as Tasmania, as well as the West Australian Current and the Southern Australian Countercurrent produced by the West Wind Drift flowing in the opposite direction. This cruise was conducted at the end of the weakest period of the Leuuwin current, which occurs from November to March.

Sea Surface Temperature (SST) of the region measured from the MODIS satellite is shown in Figure 3.5. The Polar Front can be seen at 50-55 °S and the Subantarctic Front is present just south of Australia. The maximum extent of the Leeuwin Current is seen to reach the southwest corner of the Australian mainland. The cruise track passed through the cool waters just south of the Subantarctic Front (10 to 12 °C) through to warmer coastal waters near Western Australia (18 to 20 °C), with *In situ* sea surface temperature showing a range of 11.3 to 19.7 °C.

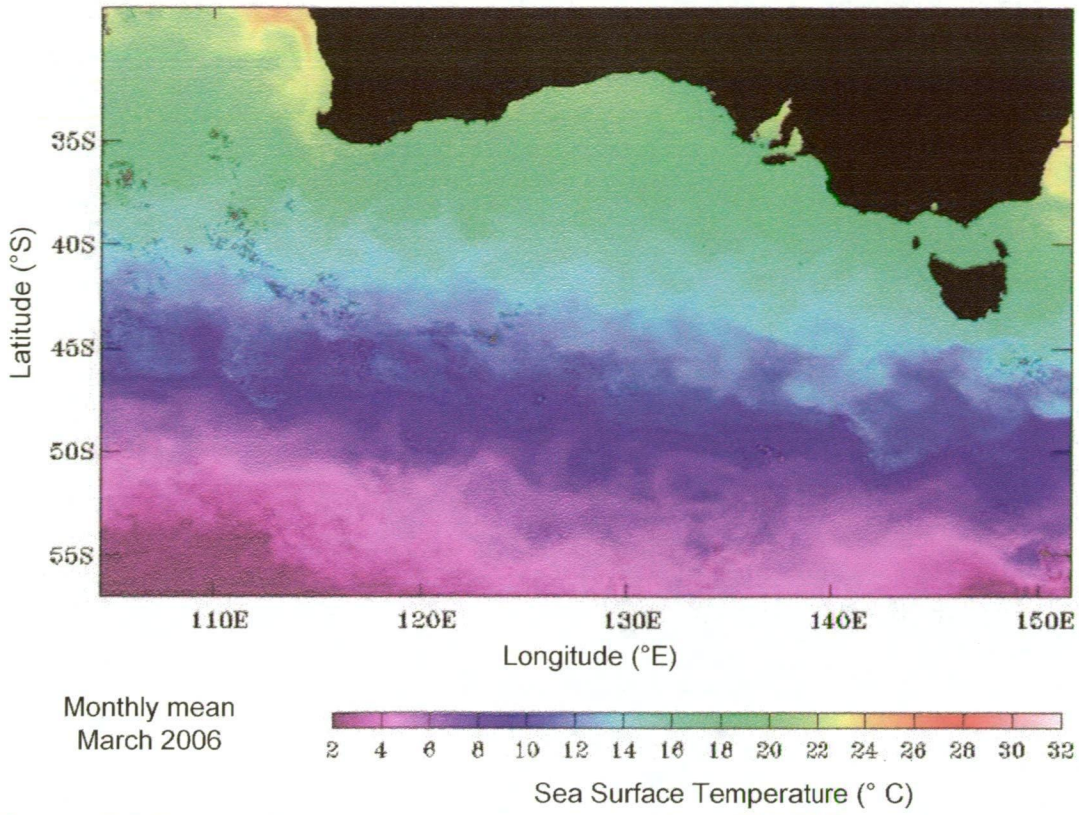

Figure 3.5 Sea surface temperature measured from MODIS satellite, monthly average for March 2006 (source: NASA Poet 2007)

3.3.2 Methyl halide concentration

Surface seawater concentration of methyl bromide was 4.2 ± 6.5 pM (range 0.3 to 31.3 pM, Figure 3.6), and methyl iodide was 2.7 ± 5.3 (range 0.05 to 25.4 pM, Figure 3.7). Both methyl halides were in higher concentration near the coast and lower in the open ocean. To test the validity of separating the measurements into three groups, a Student's T-test was applied. This showed that the measurements in the open ocean were significantly different to the measurements in the Tasmanian transect ($p = 0.004$ for methyl bromide, $p = 0.009$ for methyl iodide) and reasonably different to the measurements in the Western Australia transect ($p = 0.04$ for methyl bromide, $p = 0.046$ for methyl iodide).

Methyl bromide and methyl iodide concentration decreased with distance from shore in both transects, and the effect was stronger near Tasmania (Figure 3.8, 3.9). When combined, these measurements show an approximate logarithmic relationship with distance from shore, with indicative but not significant correlations for methyl bromide ($R^2 = 0.61$) and methyl iodide ($R^2 = 0.75$).

In the surface waters of the open ocean off the continental shelf, methyl bromide concentration was 1.5 ± 1.0 pM (range 0.3 to 4.4 pM), which is similar to previous measurements (Table 3.1). Methyl iodide concentration in open ocean seawater was 0.55 ± 0.5 pM (range 0.05 to 1.4 pM), which is in the lower range of previous measurements (Table 3.1).

Table 3.1 Measured methyl halide concentrations in surface seawater in the open ocean from various locations

Region	Methyl bromide (pM)	Methyl iodide (pM)	Reference
Southern Ocean near Aus.	0.3 - 4.4	0.05 – 1.4	This study
Southern Ocean 45-65 °S	0.5 - 2		Yvon-Lewis *et al.* 2002
Atlantic Ocean	2 - 8		Baker *et al.* 1999
80 km off Cape Grim	2.1, 8.1		Sturrock *et al.* 2003
Labrador Sea		< 2.5	Moore & Groszko 1999
Tropical Atlantic		4 - 6	Richter 2003
Atlantic		≤ 8.5	Tanzer & Heumann 1992
Off Ireland		≤ 6	Baker *et al.* 2000, Moore & Groszko 1999
Atlantic, 19 °S		≤ 12	Happell & Wallace 1996
Tropical Pacific		≤ 48	Singh *et al.* 1983
Off South Shetland Is.		≤ 53	Reifenhauser & Heumann 1992
Atlantic Ocean (Fig 1.6)		0.25 - 18.68	Chuck *et al.* 2005
Pacific Ocean (Fig 1.6)		2 - 6	Moore & Groszko 1999
North Atlantic (Fig 1.7)		~2	Smythe-Wright *et al.* 2006

An unexpectedly high concentration of methyl iodide was found in one station in the open ocean, well away from coastal influence. An anomalous high concentration of methyl iodide was previously measured 500 km off New Zealand (Moore & Grozsko 1999). Assuming this was not due to experimental error, these measurements may reflect small regions of ocean with anomalous high concentrations of methyl halides,

with an as yet unknown cause. Cohan *et al.* (2003) noted a strong source region of methyl iodide in the Tasman Sea, detected through back trajectories of air parcels at Cape Grim.

Methyl halide concentration with depth was measured in a limited number of samples in several CTD casts (see Figure 3.5). The measurements (Figure 3.10 & 3.11) indicated no consistent trend of methyl halide concentration with depth. There were more profiles showing a sub-surface maximum than those with a surface peak for both gases. There is insufficient data to map the depth profile of the gases across this region of ocean, however this limited data suggests that there may be sub-surface peaks in methyl iodide concentration similar to those found in the north Atlantic Ocean at approximately 50 to 60 °N by Smythe-Wright *et al.* (2006), and that the sub surface peaks are spatially variable.

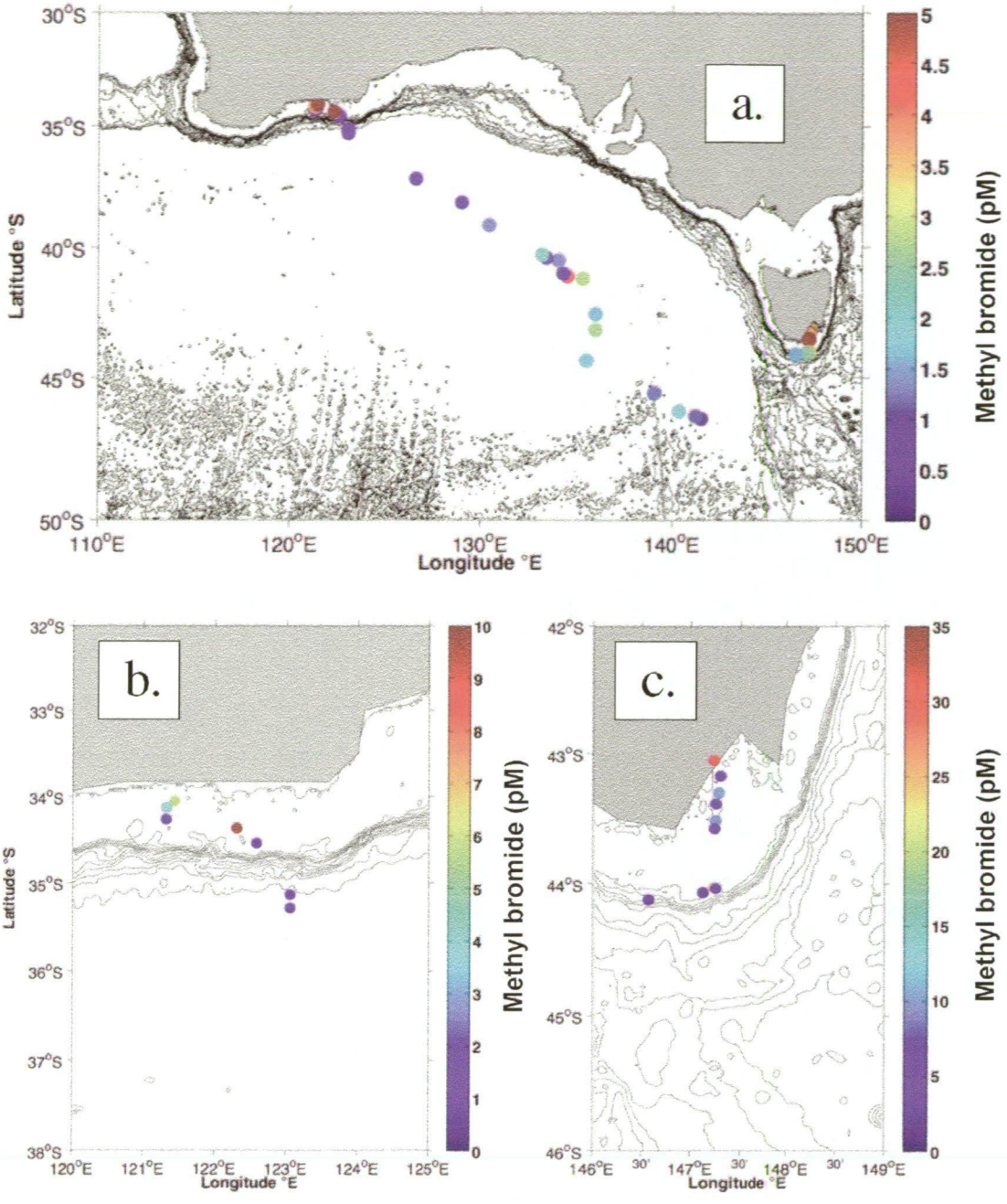

Figure 3.6 Methyl bromide concentration in surface seawater (a) measurements between Tasmania and Western Australia, close-up of (b) measurements near WA and (c) measurements near Tasmania (contours show bathymetry, to indicate the position of the continental slope)

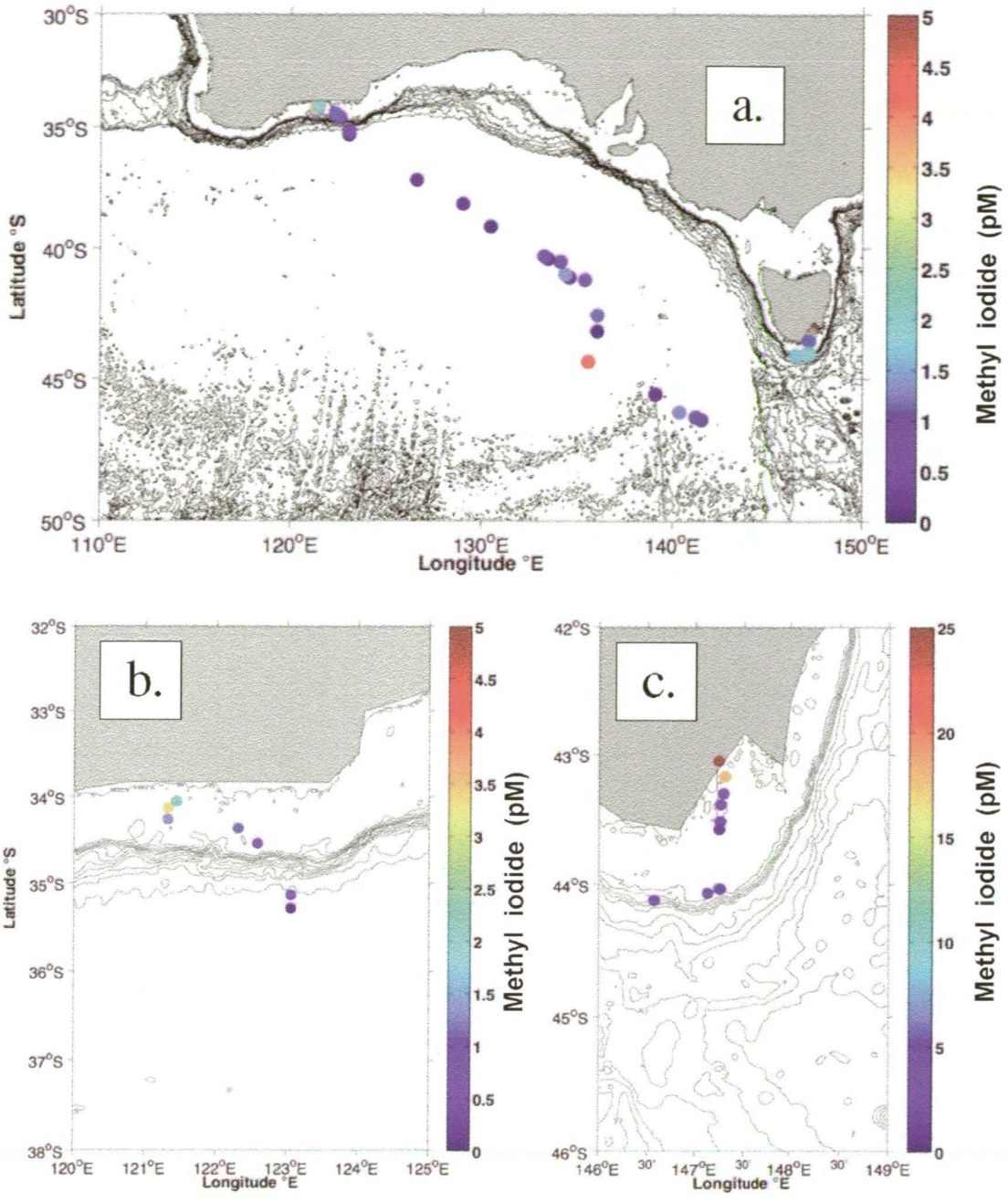

Figure 3.7 Methyl iodide concentration in surface seawater (a) measurements between Tasmania and Western Australia, with a close-up of (b) measurements near WA and (c) measurements near Tasmania (contours show bathymetry, to indicate the position of the continental slope)

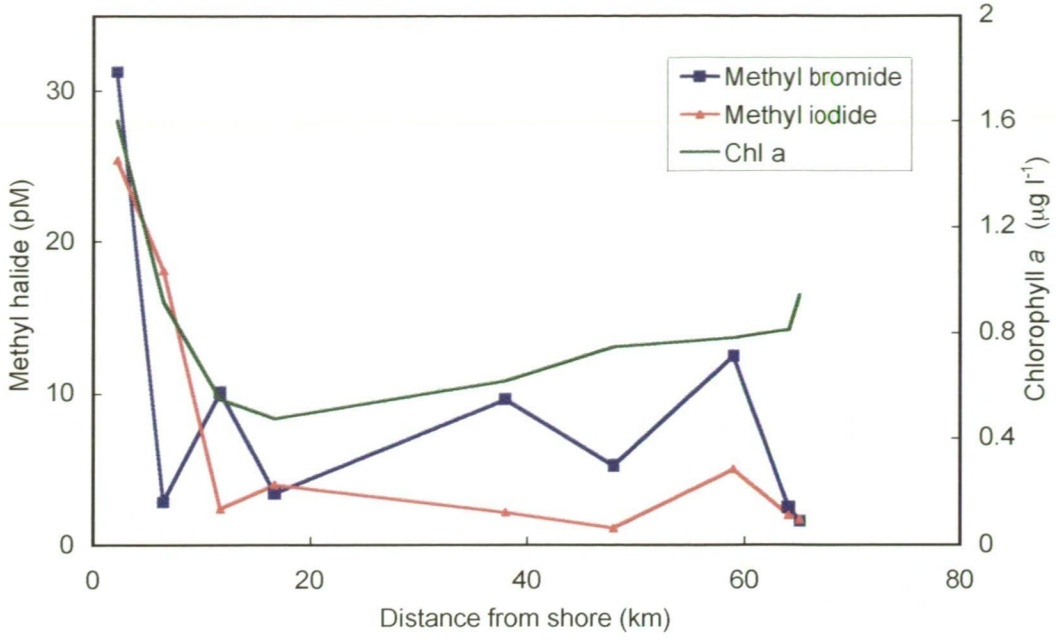

Figure 3.8 Surface seawater concentrations of methyl bromide, methyl iodide and Chlorophyll *a* south of Tasmania (initial 10 measurements)

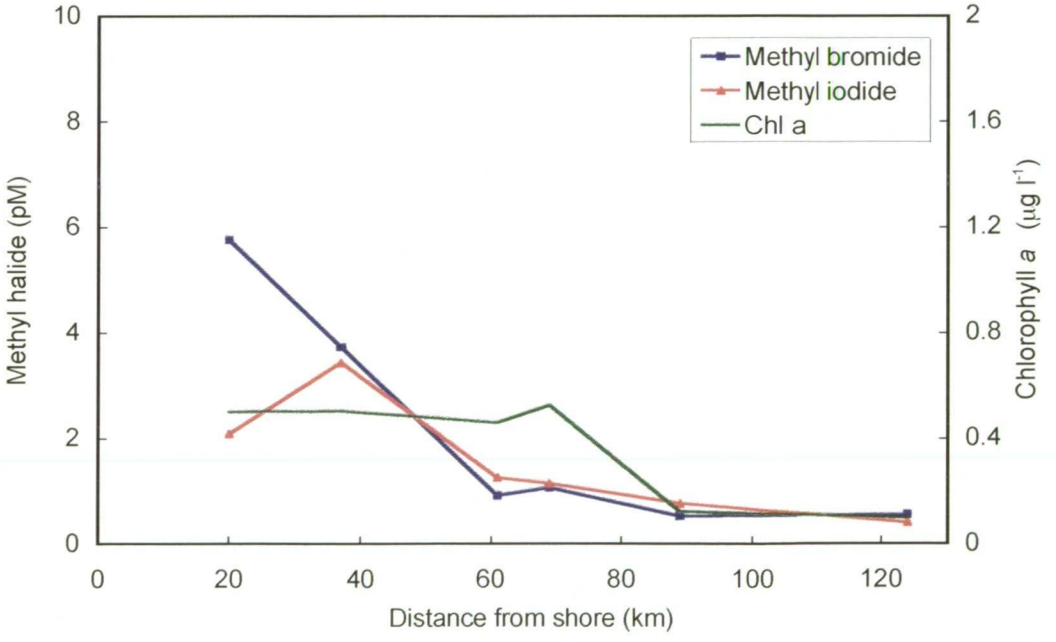

Figure 3.9 Surface seawater concentrations of methyl bromide, methyl iodide and Chlorophyll *a* south of Western Australia (final 6 measurements)

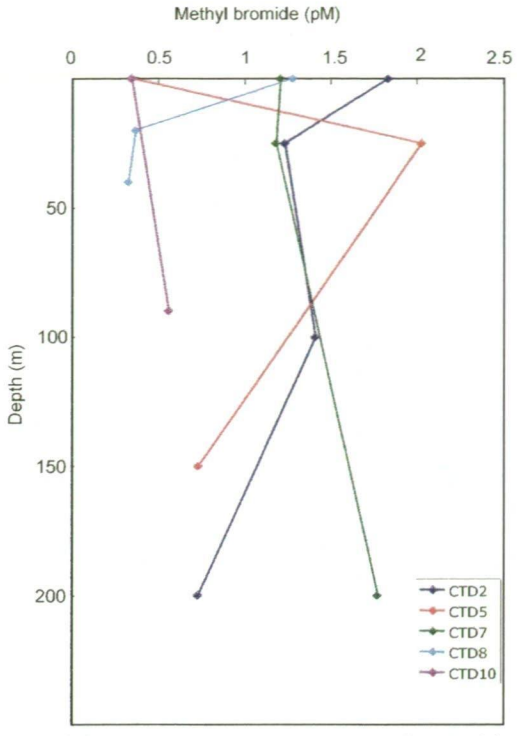

Figure 3.10 Methyl bromide seawater concentration with depth in the open ocean south of Australia, measured in CTD casts (CTD number shown)

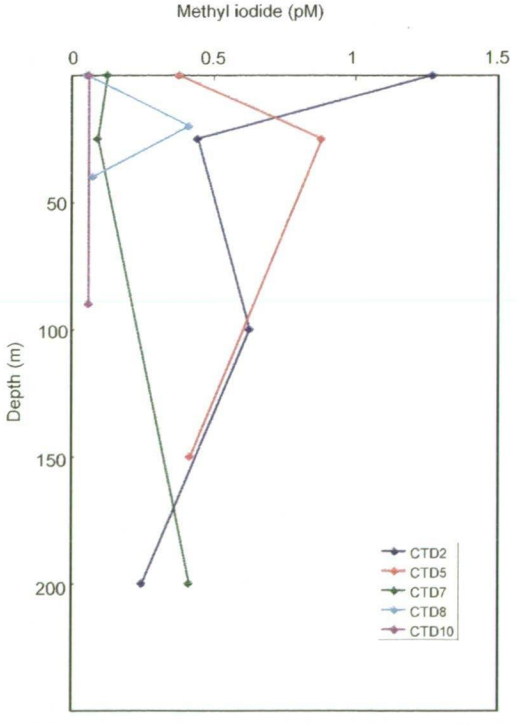

Figure 3.11 Methyl iodide seawater concentration with depth in the open ocean south of Australia, measured in CTD casts (CTD number shown)

3.3.3 Methyl halide saturation

Estimations of methyl halide saturations were made using the equations outlined in Chapter 1 and assumed the air concentration was equivalent to that of the average baseline measurements made at Cape Grim during the same period (8.1 pptv for methyl bromide, 1.5 pptv for methyl iodide). These are not considered precise measurements, but are given to illustrate the sign and order of magnitude of the saturation.

Along the Tasmanian transect, methyl bromide saturation fell from >2000% near the shore to ~100% offshore and methyl iodide saturation fell from >7000 % near the shore to 500% off shore. Approaching the Western Australia coast methyl bromide saturation increased, reaching a maximum of ~800% and methyl iodide saturation increased, peaking at ~1000%.

In the open ocean off the continental shelf, methyl bromide saturation averaged 92 ± 62% (range 19 to 272%), which indicates that the region of open ocean is close to equilibrium and may act as a very minor net sink of methyl bromide at the time of sampling. This measurement is higher than the measurement of 61% (an under-saturation of –39 ± 11%) made in the Southern Ocean further south (Yvon-Lewis *et al.* 2004). It is similar to the finding of minor under-saturations found in the Southern, Atlantic and Pacific Oceans by Lobert *et al.* (1995, 1996, 1997) and Moore & Webb (1996). Methyl bromide saturation appears to be consistent with previous findings regarding the relationship to temperature (discussed below).

Methyl iodide saturation in the open ocean averaged 173 ± 170% (range 16 to 467%), with most measurements above 100% equilibrium and some below. This indicates the region is probably a minor net source region of methyl iodide at the time of sampling. This is consistent with the finding of positive saturation in large areas of the world's oceans, including the waters of the northwest Atlantic, northeast Atlantic and the Pacific Ocean (Moore & Groszko 1999).

However, the errors from the analysis method (±1-40%) and the assumption of air concentration as baseline at Cape Grim mean that the calculation of saturation is not precise. The sign of the average flux can't be reliably estimated for the methyl

bromide, but it appears to be positive with a small value for methyl iodide, indicating that it is a source region.

To give some perspective on how these saturations relate to sea to air flux, the wind speed over the ocean calculated from satellite measurements is shown for March 2006 (Figure 3.12). The figure depicts a time series from 1 to 31 March 2006 of the longitude-averaged wind speeds for 110-150 °E measured by satellite (NASA Quikscan product, from NASA Poet 2007). A fairly consistent latitudinal pattern is found, with lower average wind speed north of 45 °S (5 to 10 m s^{-1}) and higher wind speed south of 45 °S (10 to 15 m s^{-1}). Since the transfer velocity of gas flux has a cubic function with wind speed (Liss & Merlivat 1986, Wanninkhof 1992), this difference leads to a large difference in flux rates, up to an order of magnitude higher in the windier southern region for the same given concentration anomaly.

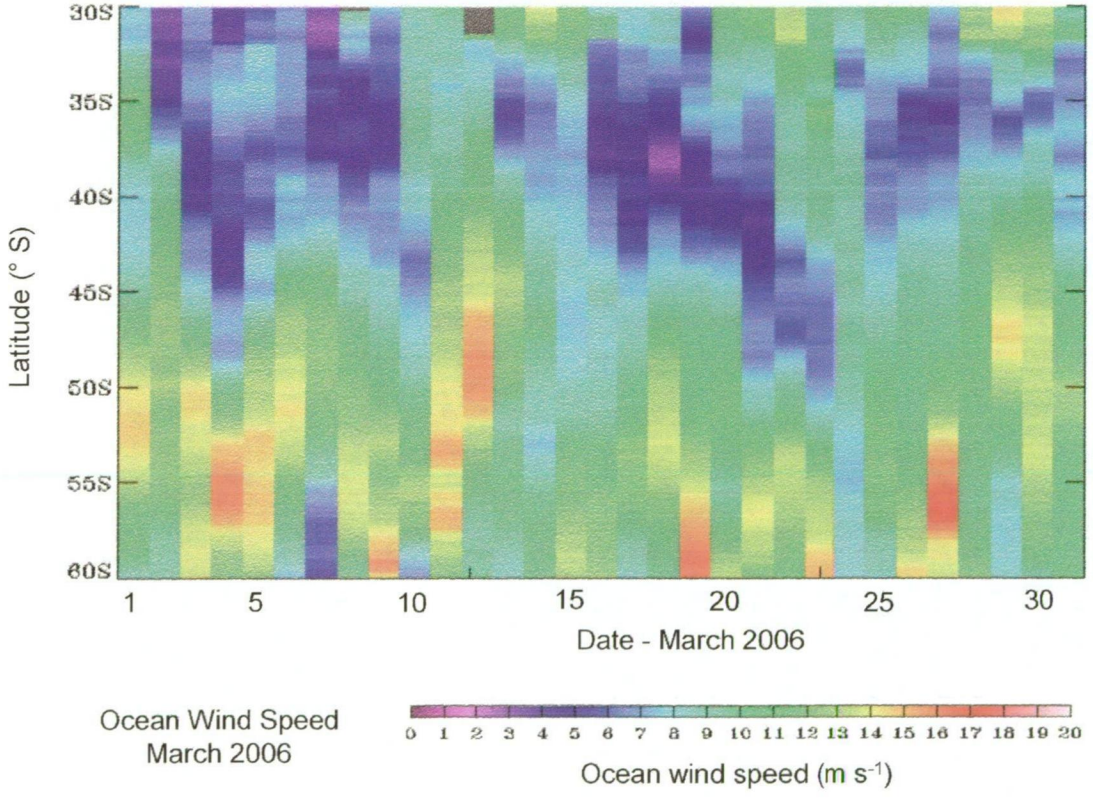

Figure 3.12 Wind speed at 10 m above the sea surface south of Australia, longitude averaged (110-150 °E) for each day in March 2006, from satellite data (source: NASA Poet 2007)

3.3.4 Methyl halide saturation and temperature

The estimated methyl bromide saturation from the open ocean measurements was 92 ± 62% (range 19 to 272%). This is generally lower but similar to the predicted methyl bromide saturation using the quadratic equations based on SST for temperate waters in Autumn given in King *et al.* (2002) shown in Figure 3.13. These saturations are also similar, but slightly lower than the saturations in the Pacific and Atlantic Oceans used to generate the equations in King *et al.* (2002) at this latitude (Figure 3.14). The peak in methyl bromide saturation appears to occur at a lower temperature than the predicted saturation maximum. However, based on this small dataset, there is no strong evidence to propose alterations to relationship between methyl bromide to SST proposed by King *et al.* (2002).

Chuck *et al.* (2005) found a strong linear correlation between temperature and seawater methyl iodide concentration through the Southern Ocean down to the sea ice margin ($R^2 = 0.87$). No such strong linear trend was found in this data ($R^2 = 0.02$). This may be because the latitudinal and temperature range of this study was much less.

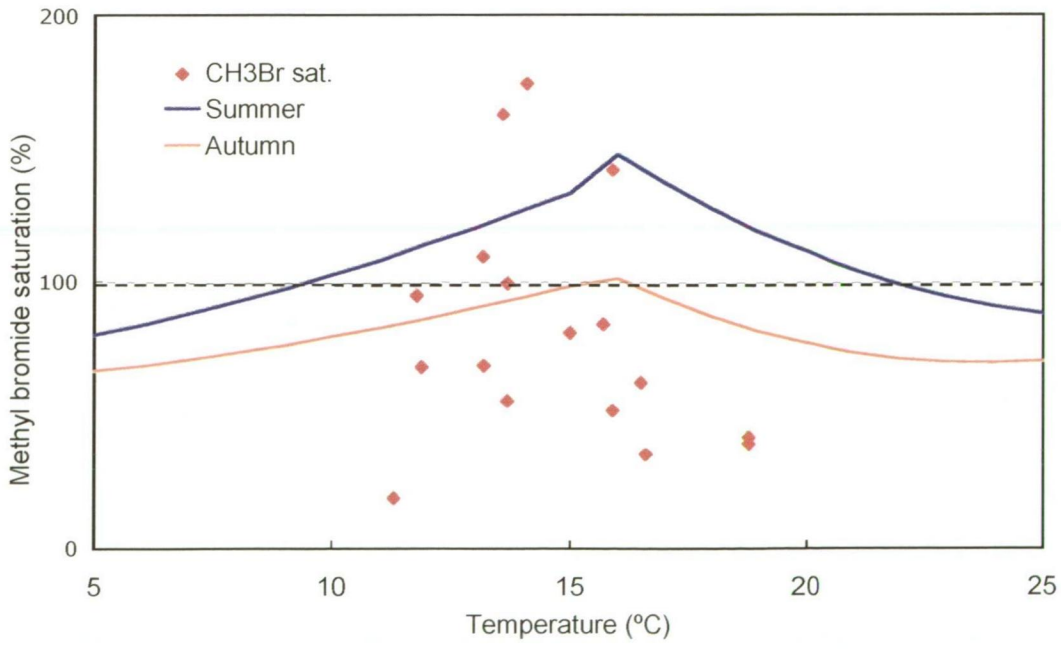

Figure 3.13 Measured methyl bromide saturation (red diamonds) in the open ocean south of Australia in early Autumn (largest outlier point off scale), and predicted methyl bromide saturation in summer and autumn (lines) calculated by equations based on sea surface temperature (King *et al.* 2002)

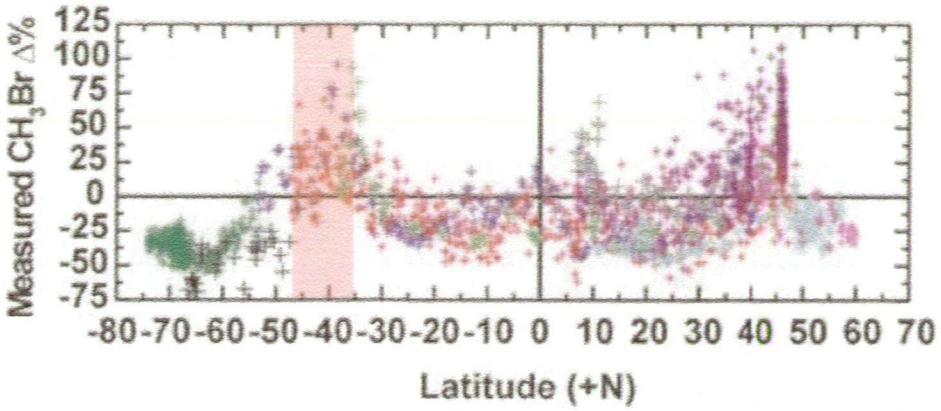

Figure 3.14 Open ocean methyl bromide saturation anomalies (difference from 100%) with latitude, measured on six cruises from King *et al.* (2000), orange shading indicates the approximate latitude range in this study

3.3.5 Correlation to phytoplankton

Surface Chlorophyll *a* measured by MODIS satellite is found in Figure 3.15 (please note non-linear scale to show detail at the lower range). The image shows high Chlorophyll *a* waters near Tasmania at the start of the voyage (up to 1 μg l^{-1}), a region of moderate Chlorophyll *a* in the southern region 38-42° Latitude that the ships track passes around, and a patch of low Chlorophyll *a* between 35-38° Latitude near the end of the voyage.

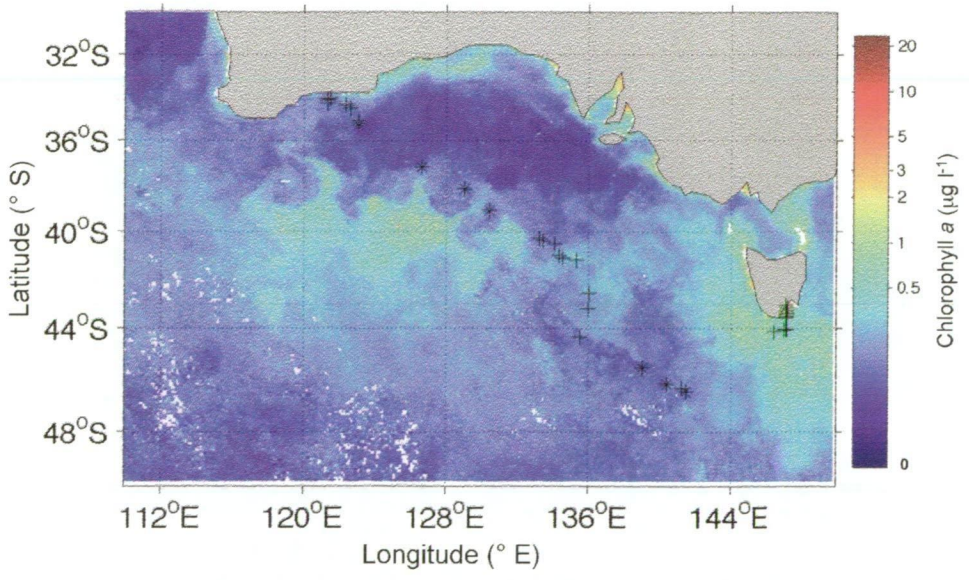

Figure 3.15 Seawater Chlorophyll *a* concentration measured from MODIS satellite, monthly average for March 2006, showing sampling sites

In situ Chlorophyll *a* and other phytoplankton pigment concentrations from each surface sampling site are compared to methyl halide concentration for evidence of a biological source (Figure 3.16). Examining all measurements, there is a broadly positive but not statistically significant linear trend of methyl halide concentration and phytoplankton biomass measured by Chlorophyll *a* (Figure 3.17).

However, this relationship is confounded by the effect of the coast on measurements made over the continental shelf. No trend is evident between methyl halide concentration and *in situ* Chlorophyll *a* in samples from only the open ocean (Figure 3.18). No significant linear correlation could be found between methyl halide concentration and any other pigment (R^2 fit are all < 0.6). Methyl iodide was not correlated well with divinyl-Chlorophyll *a*, which is a proxy for *Prochloococcus* (R^2 = 0.09). This contrasts with the significant relationship between methyl iodide and *Prochlorococcus* found in the larger and deeper dataset of Smythe-Wright *et al.* (2006). Only a weak correlation was found between methyl bromide concentration and hexanoyloxyfucoxanthin, which is a proxy for *Phaeocystis* (R^2 = 0.52). This contrasts to the finding of a significant correlation between methyl bromide and this pigment in the north Atlantic (Baker *et al.* 1999).

An instantaneous measure of phytoplankton biomass (Chlorophyll *a* concentration) may not be the most appropriate measure of biological production of methyl halide gases, since the biological production mechanism has numerous complexities and may feature a lag time, as outlined in Chapter 1 & 2. For this reason, comparison of the methyl halide concentration is compared to the modeled monthly mean net primary production from the nearest ocean grid square from MODIS satellite data as outlined in Chapter 2 (Figure 3.19). No significant trend is present here either for methyl bromide or methyl iodide.

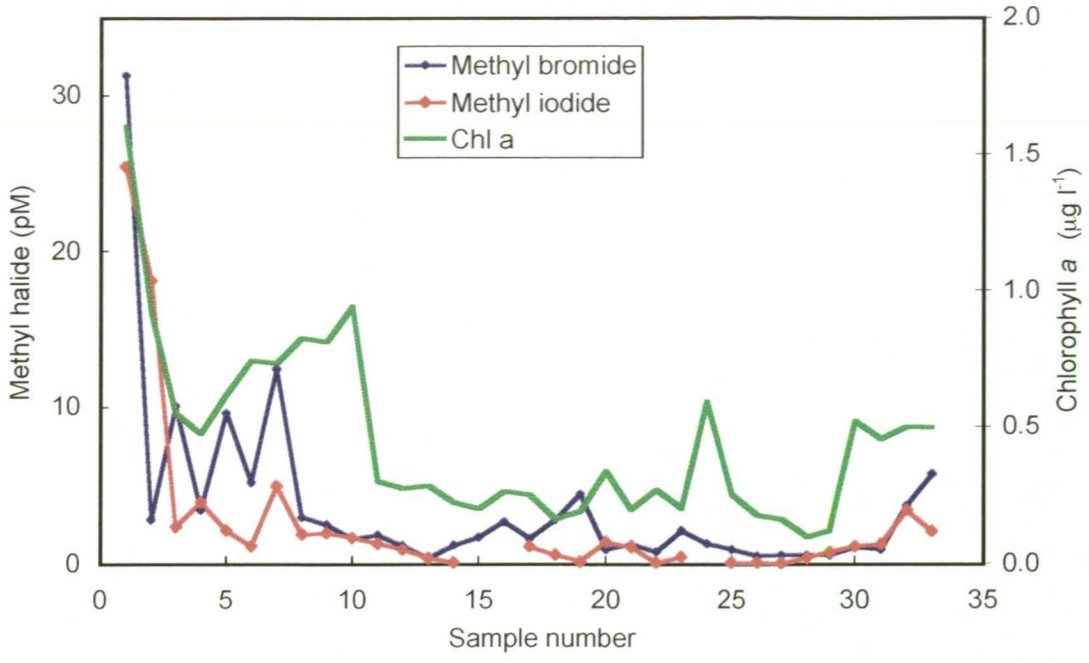

Figure 3.16 Methyl iodide and Chlorophyll *a* concentration in surface seawater measured at each sampling site across the study area

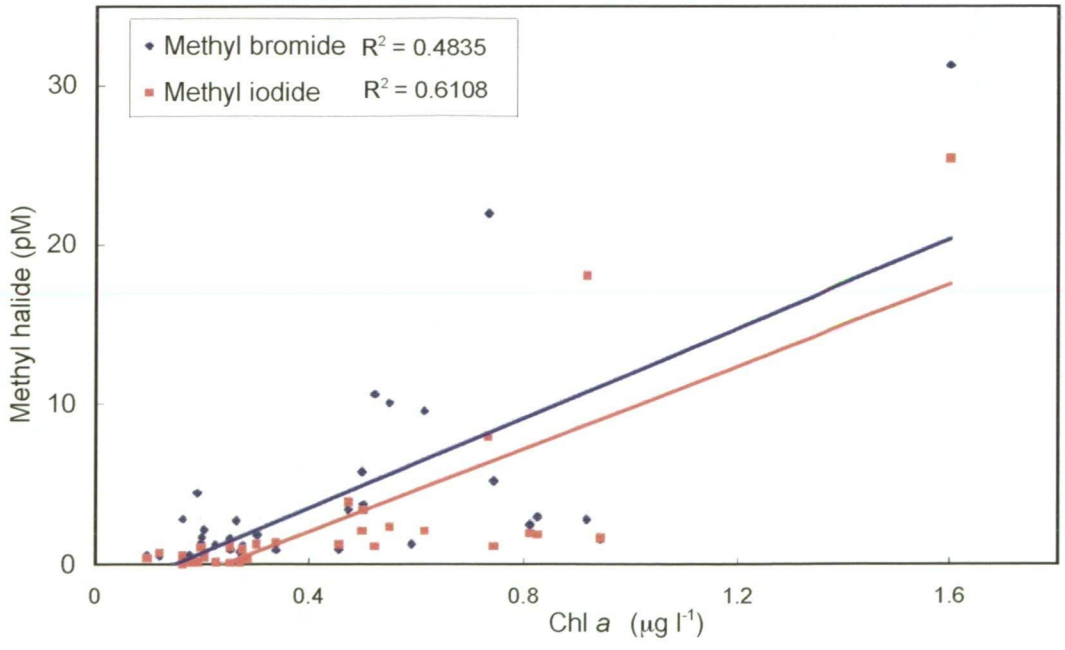

Figure 3.17 Methyl bromide and methyl iodide concentration in surface seawater measured at each site plotted against in situ Chlorophyll *a* concentration in the same sample, with fitted linear trend-lines

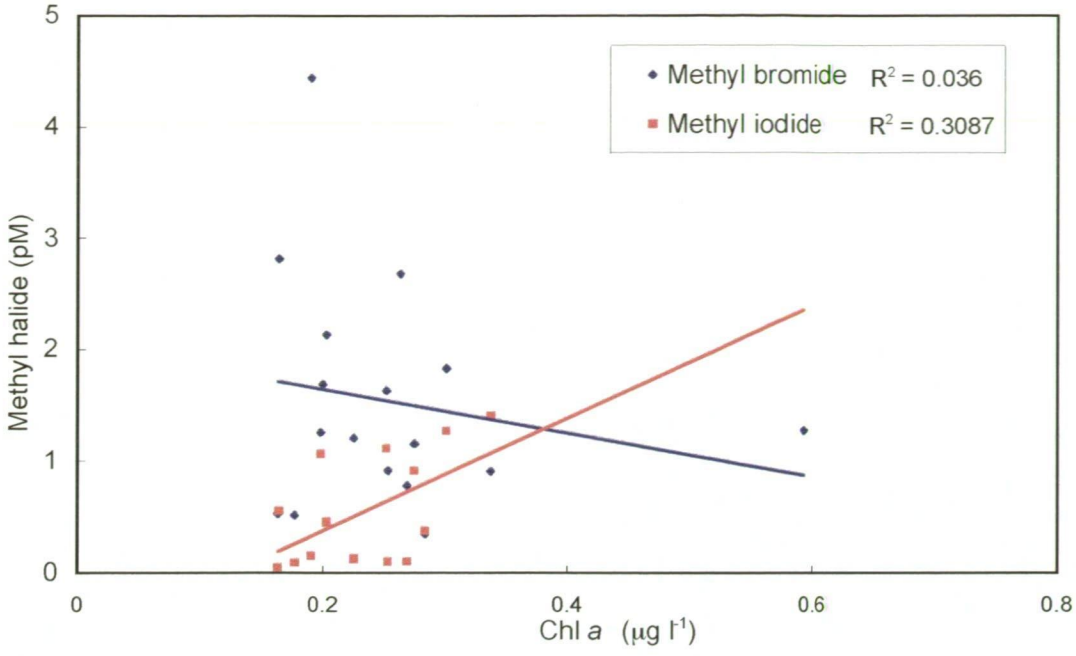

Figure 3.18 Methyl bromide and methyl iodide concentration in open ocean surface seawater south of Australia plotted against in situ Chlorophyll *a* concentration in the same sample

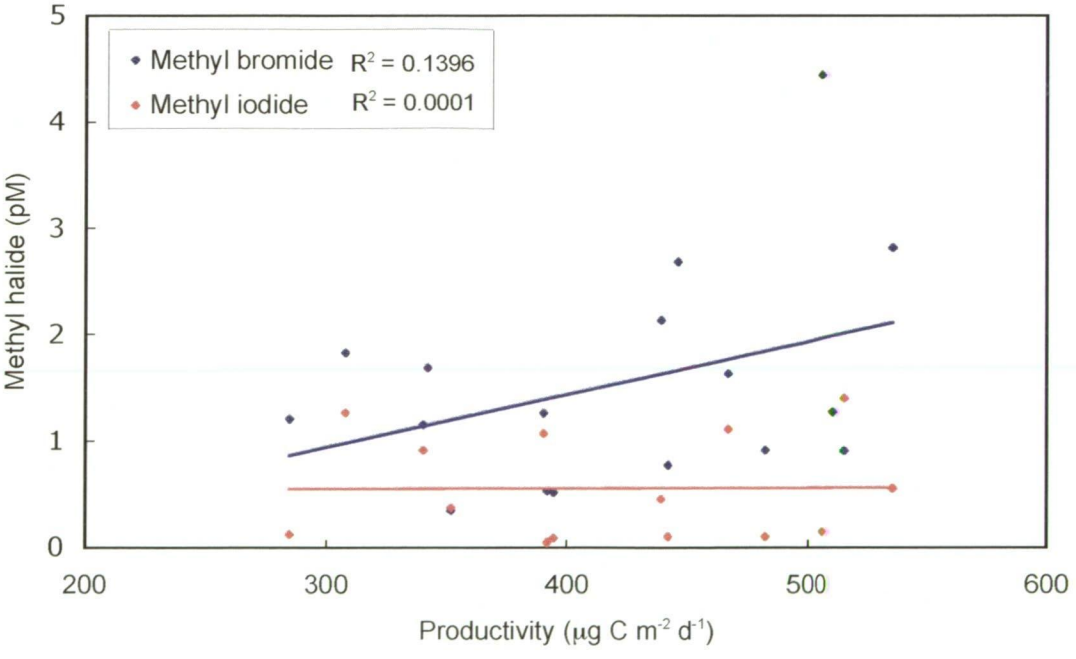

Figure 3.19 Methyl bromide and methyl iodide concentration in surface seawater from the open ocean south of Australia off the continental slope, plotted against monthly average modeled net primary production in surface waters of the relevant grid cell in March 2006

3.3.6 Inorganic iodide

Iodide concentrations were calculated semi-quantitatively in the absence of thorough evaluation of method performance and a lack of a certified reference material. Iodide was measured in underway samples and the surface samples of the CTDs. Iodide concentrations are three orders of magnitude higher than methyl iodide (Figure 3.20). There is a broadly positive relationship between iodide and methyl iodide in surface seawater (Figure 3.20, 3.21). This relationship is most evident close to the Tasmanian coast where both concentrations are elevated in a similar pattern (e.g. sampling station 7). The broadly positive correlation between iodide and methyl iodide, particularly in relation to distance from shore, supports the hypothesis of a generally linked or synergistic production of both species.

However, this linear correlation is weak ($R^2 = 0.16$). The ratio of methyl iodide to iodide was always less than 1:5000, shown as a dashed line in Figure 3.21, with no points above this line but numerous points far below. This suggests there are some differences in the specific character of each process. This distribution also suggests that the methyl iodide production requires a minimum iodide concentration, giving this upper threshold ratio, but also requires one or more other conditions. The ratio between methyl iodide and iodide was highest in the sample closest to shore (1:5120), suggesting that the conversion of iodide to methyl iodide was enabled or promoted in coastal waters.

The relationship is consistent with biological inter-conversion of iodine species in surface water from iodate to iodide and iodide to methyl iodide, with different characteristics of each specific conversion. Biological production of methyl iodide is associated with growth of a specific suite of phytoplankton species, and rates vary with growth phase and with the influence from various conditions (see Chapter 1). Similarly, the biological production of iodide from iodate is performed by a specific suite of species, and varies with growth phase (Wong *et al.* 2002), but these are distinct from the production of methyl iodide. There are also distinct bacterial and dissimilation processes of iodide compared to methyl iodide. The net iodide levels in surface waters have been suggested to be an integration of the patchy dissimilation or regenerated production processes (Tian *et al.* 1996). Higher iodide nearer the coast is

also consistent with increased release of iodide from sediments, and coastal processes such as bacterial reduction and also conceivably from terrestrial run-off.

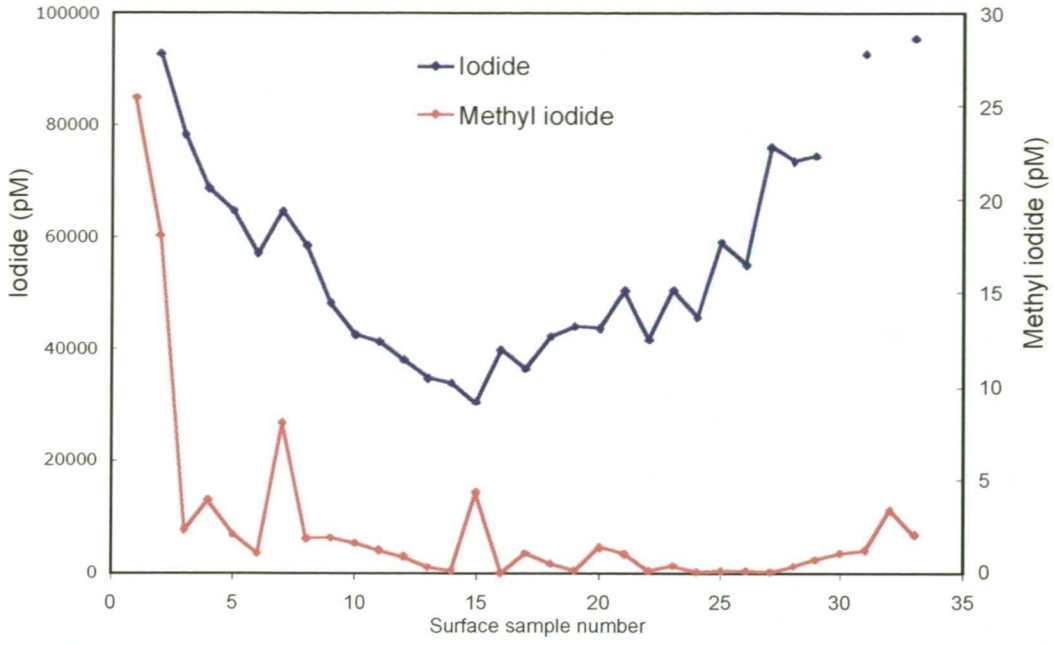

Figure 3.20 Inorganic iodide (I^-) and methyl iodide concentrations in surface seawater samples south of Australia

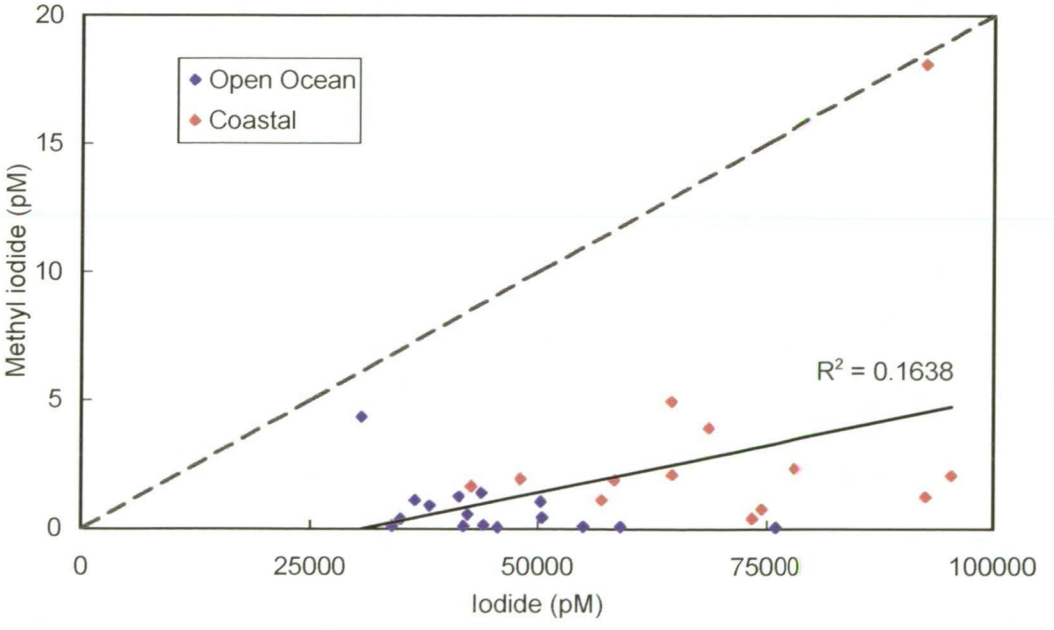

Figure 3.21 Methyl iodide and inorganic iodide (I^-) concentration in seawater south of Australia, showing linear trend line for all measurements (solid line), as well as a line representing a ratio of 1:5000 (dashed line)

3.4 Conclusions

Methyl halide concentration had a strong relationship to distance from shore, dropping from high levels near the Tasmanian coast (>20 pM) down to low levels in the open ocean (generally <2 pM). Similarly, saturation fell from strongly positive near the coast down to near equilibrium in the open ocean. The data suggest that the open ocean in this region is a minor net source of methyl iodide and a very minor net source or sink of methyl bromide at this time. Methyl bromide saturation was roughly consistent with the equations based on SST of King *et al.* (2002).

The source and sink of the methyl halides in this region of the open ocean source are expected to have an influence on the concentration measured in baseline air at the Cape Grim station. March is a time of relatively high methyl bromide and methyl iodide concentration measured at the station (Chapter 2), so this period may be the time of higher ocean source. However, no description of seasonal changes in the ocean source is possible from these limited measurements.

No clear correlation between methyl halide concentration and any photosynthetic pigment was present in the open ocean, and the relationship between the biological source of methyl halides and phytoplankton is suspected to be more complex than a simple biomass measurement will indicate. Methyl iodide concentration appears broadly correlated with iodide concentration. This pattern is consistent with a linked or synergistic production of both these species, possibly from biological inter-conversion by phytoplankton and bacteria.

Chapter 4. Production of methyl halides in the coastal waters of northwest Tasmania

4.1 Introduction

This chapter examines the production of methyl bromide and methyl iodide in the zone of coastal waters on the continental shelf of northwest Tasmania at 9 km offshore. This zone is away from the direct effect of the coast but is not in the open ocean. Sources and sinks in this region will contribute to the atmospheric concentration of methyl halides measured at Cape Grim station, and times of strong positive saturation may contribute to peaks of elevated concentration detected there. A major focus of the work described in this chapter was the analysis of temporal variability in the methyl halide source from coastal waters, particularly seasonal changes. The phytoplankton community was examined to investigate any biological sources of methyl halides.

4.1.1 Previous results from Cape Grim

Measurements of methyl halides in seawater near Cape Grim and in air at Cape Grim Baseline Air Pollution Station (CG BAPS) were initiated in 2000 by Georgina Sturrock and have run sporadically ever since. A biological component was started in 2001 to investigate the link between plankton and methyl halide emissions. An honours thesis (Corno 2001), a paper (Sturrock *et al.* 2003) and a report (Corno *et al.* 2004) have been written regarding this work thus far. Sturrock *et al.* (2003) found that the surface seawater off NW Tasmania (sites at Cape Grim and Couta Rocks) are highly supersaturated in methyl bromide throughout the year, with no evidence of any seasonal cycle. Under-saturation was found further offshore (open ocean 80 km offshore), although still under coastal influence.

Corno (2001) outlined a determination of phytoplankton community structure, environmental factors controlling phytoplankton biomass and methyl halide concentrations. Possible relationships between phytoplankton abundance and species with atmospheric and seawater concentrations of methanesulphonic acid (MSA),

methyl bromide and methyl iodide in coastal waters off Cape Grim during spring summer and autumn of 2000/01 were investigated. Based on a series of measurements over summer methyl halide concentrations, particularly methyl iodide ($R^2 = 0.89$), had a correlation to phytoplankton biomass, and changes in diatom and small flagellate abundance were closely linked to variations in methyl halide concentrations. The main conclusions drawn from this work were that phytoplankton are a source of methyl halides in these waters, in particular diatoms and small flagellates, and that production of methyl halides might have been a response to nitrate limiting conditions.

Corno *et al.* (2004) was published expanding the results in Corno (2001). They reported that seasonal phytoplankton variation at Cape Grim did not show the typical major spring bloom followed by a smaller one in autumn, instead it showed a major autumn bloom. Chlorophyll *a* concentration was measured to be 0.05 to 1.1 $\mu g\ l^{-1}$, similar to open ocean and less like sheltered coastal waters. Corno *et al.* (2004) also found seawater methyl bromide concentrations were not correlated with those in air collected at the same time in the same place. Atmosphere samples collected under onshore (baseline) and offshore conditions showed the same variability according to regional & land based sources of methyl bromide as Cox (2001) and Sturrock *et al.* (2001). A significant correlation between seawater concentration of methyl bromide and N:P ratio was found, showing a strong inverse relationship. Indicative but not statistically significant relationships were found between methyl bromide concentration and the biomass of dinoflagellates, small flagellates, diatoms, and phytoplankton overall.

4.2 Site description – Couta Rocks

Samples were taken at a site 9 km offshore from Couta Rocks (Figure 4.1). Couta Rocks is a small fishing village on the west coast of Tasmania, approximately 45 km south of the Cape Grim station. This coast is exposed to high wave action and swell, but with a small tidal range. Onshore air at Couta Rocks is from a very similar back trajectory to that arriving at the Cape Grim station and was considered baseline. The coast is made up of rocky reefs interspersed with sandy beaches. The inter-tidal zone

of these rocky reefs almost exclusively contains bull kelp (*Durvillaea potatorum*) and there are considerable amounts of beach-cast kelp on the sandy beaches. An industry of beach-cast kelp collection exists in the area for the production of liquid fertilizer. Samples were taken at 9 km offshore to avoid the influence of these kelp beds.

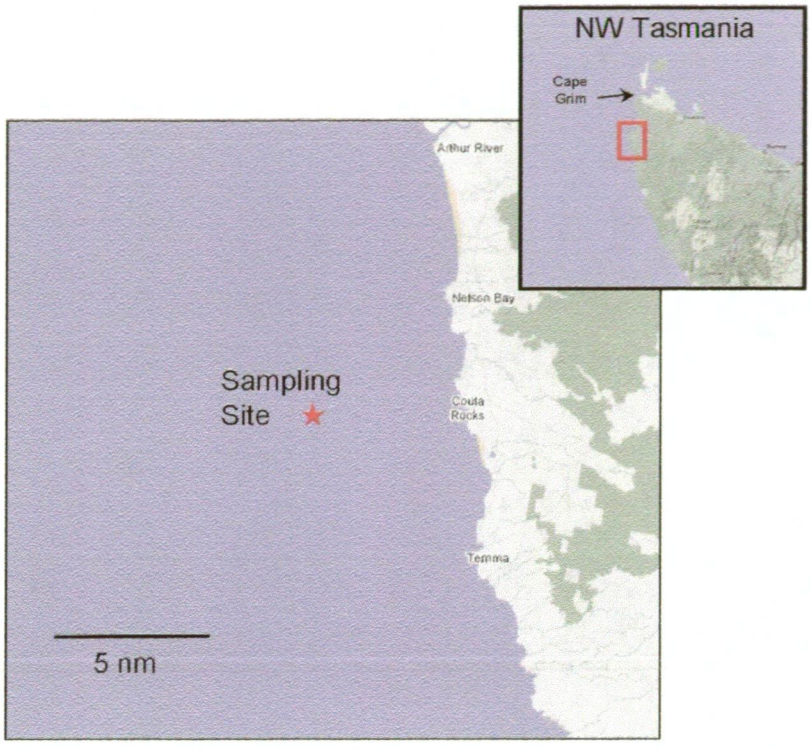

Figure 4.1 Map of northwest Tasmania, showing the location of Couta Rocks, and the coastal waters sampling site (source: Google maps)

4.3 Methods

Seventeen sampling trips were made between January 2003 and January 2006 (6 in 2003, 6 in 2004, 4 in 2005, and 1 in 2006). Bureau of Meteorology technician Bob Parr assisted with the methyl halide sampling and analysis. Research assistant Chris Lane conducted water column sampling and analysis from January 2003 to February 2004, and all subsequent samples analysed personally. Sampling trips were concluded in January 2006 when analysis equipment failed.

4.3.1 Methyl halide sampling

To sample air, a six litre stainless steel glass-lined flask was first flushed and then filled to a pressure of 1.6 bar with a battery operated pump. The inlet was directed upwind of the vessel to avoid contamination. A surface seawater sample was collected using a bucket, two 100 ml glass syringes were flushed with seawater before being filled and sealed. The syringes were kept on ice in the dark before analysis.

Water samples were analyzed within six hours of collection and air samples were analyzed within a month of collection. Water and air samples were analyzed for concentration of methyl bromide and methyl iodide by GC-ECD. All samples were quantified against a known primary air standard. A full description of the method is found in Sturrock *et al.* (2003), and is based on Baker *et al.* (1999, 2001). Saturation of methyl halide between the ocean and atmosphere was calculated using the formulae outlined in Chapter 1.

4.3.2 Water column sampling

Light transmittance was assessed using a Secchi disk measurement. An approximate attenuation coefficient (K_D) is calculated from this using Equation 4.1, and a 1% light compensation depth (Z_C) is calculated using Equation 4.2. The compensation depth can occur between 0.1 to 20% of surface light, however 1% light is a commonly accepted convention. This calculation of compensation depth accepts the validity of the Beer-Lambert Law where ln(0.01) = -4.6.

$$K_D = f/Z_S \quad (4.1)$$

K_D = attenuation coefficient
Z_S = Secchi disk depth
f = dimensionless conversion factor, 1.4 for turbid coastal waters

$$Z_C = (4.6)/K_D \quad (4.2)$$

Z_C = compensation depth

Temperature and salinity profiles to 20 m depth were taken using a portable Platypus Instruments CTD. Temperature of the surface water was also measured using a mercury thermometer.

Water samples were taken at 0, 5, 10 and 20 metres depth using a Niskin sampler. Sub samples from each depth were taken as follows: one litre for Chlorophyll *a* analysis, one litre for cell counting and 2 x 10 ml for nutrient analysis. Samples for cell counting were immediately spiked with 1 to 2 ml of Lugol's iodine solution to preserve cells and all samples were immediately placed on ice in the dark before analysis.

Within two hours, the seawater samples for Chlorophyll *a* analysis were filtered onto a Whatman 47 mm GF/F filter using a Niskin polycarbonate filter chamber attached to a diaphragm pump, filters were then stored in a -80 °C freezer before analysis. Pigments were extracted in 10 ml of methanol for at least 8 hours, and immersion in a sonic bath for 10 minutes. Chlorophyll *a* was measured in the extract by the acidification method (Holm-Hansen and Riemann 1978) using a Turner Instruments 10 AU digital fluorometer.

Within two weeks, samples spiked with Lugol's iodine solution were reduced from 1000 ml to 10 ml via settling. Cell counts were conducted on at least 0.25 ml of the reduced solution (representing 25 ml of original sample) using a Zeiss Televar inverted microscope. Phytoplankton cells were identified only to major group level; diatoms, dinoflagellates, *Phaeocystis* sp. colonies, other small flagellates, coccolithophorids and chlorophytes. Ciliates (photoautotrophic protistans) and copepod larvae were also counted. Picoplankton, bacterioplankton or nanoplankton were not enumerated.

The 2 x 10 ml samples were frozen immediately and stored in a freezer at –20 °C before analysis for nutrients within three months. Concentration of the major macronutrients of phosphate, silicate and nitrogen (nitrate and nitrite) were measured. In 2003, nutrients were measured using an ALPKEM autoanalyser, subsequent measurements were made using a Lachat QuickChem 3000 auto-analyzer (standard QuickChem methods).

4.3.3 Satellite data

SST, Chlorophyll *a* and PAR from MODIS satellite were examined, along with NPP modeled from the above variables. These data were obtained from Oregon State University Ocean Productivity project (2007). Monthly averaged data for Box 2 is used, covering the region of coast of northwest Tasmania (see Chapter 2 for a description).

4.4 Results

4.4.1 Physical conditions

Water temperature, salinity and compensation depth are shown in Figure 4.2. Water temperature averaged 15.4 ± 1.3 °C over the period (a summer maximum of 17.1 °C, a winter minimum of 12.7 °C). Salinity averaged 34.4 ± 0.3 (range 33.8 to 34.7) with no clear seasonal cycle. Compensation depth varied greatly throughout the year, with a winter maximum (July 2003, May 2004, September 2005). A particularly high compensation depth was present in May 2004.

Nutrient concentrations were similar to the open ocean. The sum of nitrate and nitrite (NO_3^- + NO_2^-) averaged 0.91 ± 1.2 μmol l^{-1} (range 0.02 to 4.26 μmol l^{-1}), phosphate averaged 0.19 ± 0.13 μmol l^{-1} (range 0.03 to 0.42 μmol l^{-1}) and silicate averaged 1.1 ± 0.52 μmol l^{-1} (range 0.28 to 2.11 μmol l^{-1}). Nitrate + nitrite to phosphate ratio averaged 5.2 ± 3.8 (range 0.1 to 10.7), which is consistently below Redfield ratio, indicating that the waters are more likely to be limited by nitrogen than phosphate. Nitrate + nitrite was generally higher in the early part of 2003, and showed another peak in September 2005.

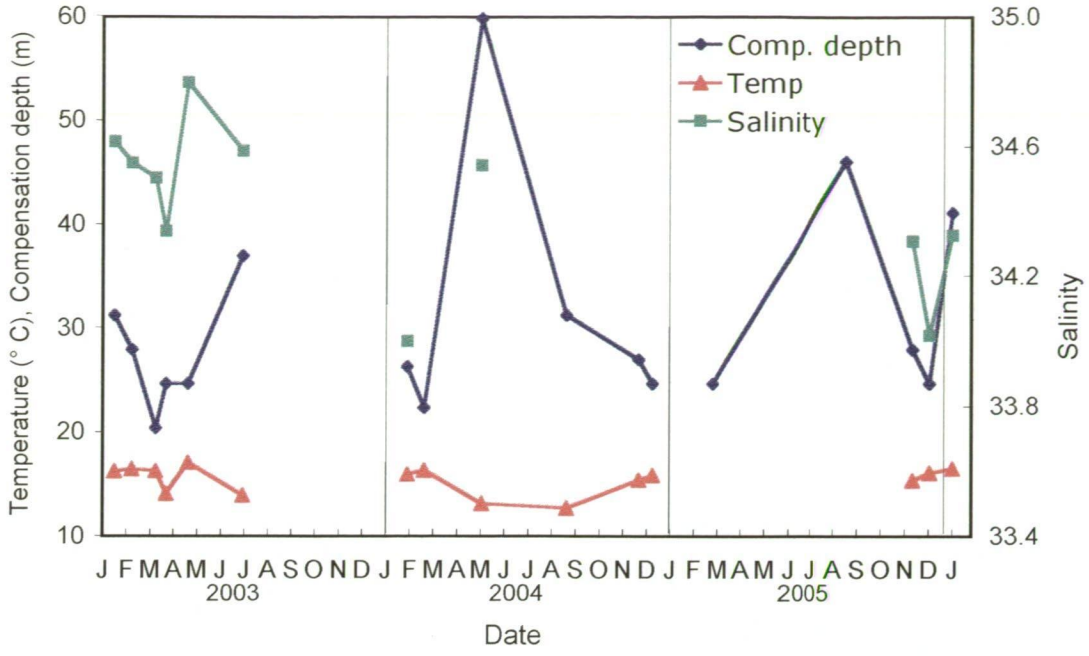

Figure 4.2 Surface seawater temperature, average salinity (0-20 m) and compensation depth calculated from Secchi Disk measurement at a sampling site 9 km offshore from Couta Rocks Tasmania 2003-2006

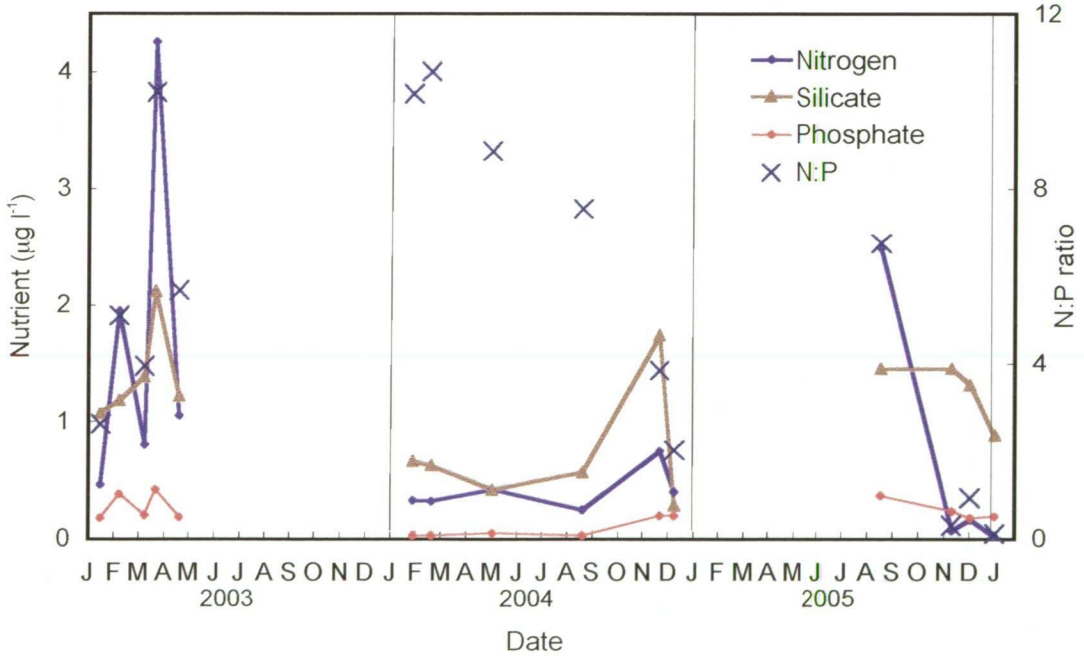

Figure 4.3 Macronutrient concentrations and nitrate + nitrite to phosphate ratio in seawater measured 9 km offshore from Couta Rocks, NW Tasmania

4.4.2 Phytoplankton

The biomass of the phytoplankton community expressed as Chlorophyll *a* concentration was examined in two ways; through *in situ* sampling and satellite data. Community composition was examined through cell counts from field samples.

In situ Chlorophyll *a* concentration was from 0.16 to 1.5 μg l^{-1} (average 0.62 ± 0.38 μg l^{-1}) and phytoplankton cell counts were between 8,000 and 170,000 cells l^{-1} (average 70,000 ± 50,000 cells l^{-1}) (Figure 4.4). Both peaked in the warmer months, but did not show a predictable or consistent annual trend. Monthly average Chlorophyll *a* concentration for Box 2 estimated from ocean colour from MODIS satellite shows some of the trends between sampling times (Figure 4.5).

Examining the species information, the community contained a large number of *Phaeocystis* sp. colonies, commonly containing 20 to 50 cells. A notable succession of species occurred in spring to summer 2004, with a peak in large dinoflagellates occurring in late August followed by a large peak in diatom numbers into December (Figure 4.6).

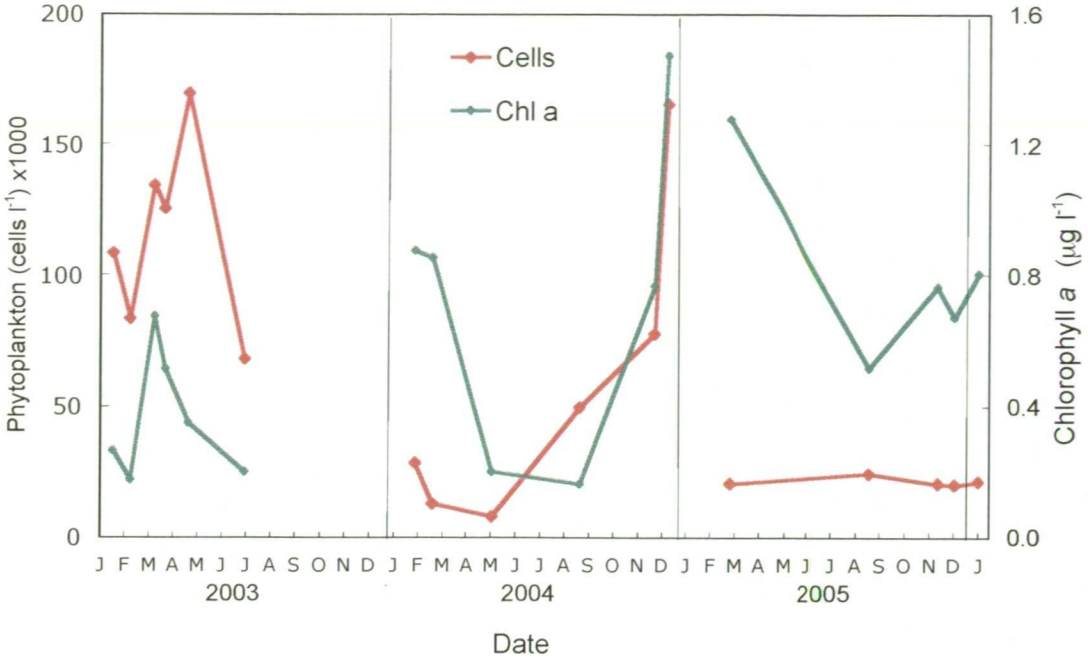

Figure 4.4 Chlorophyll *a* concentration and phytoplankton cell counts in surface seawater 9 km offshore from Couta Rocks, NW Tasmania

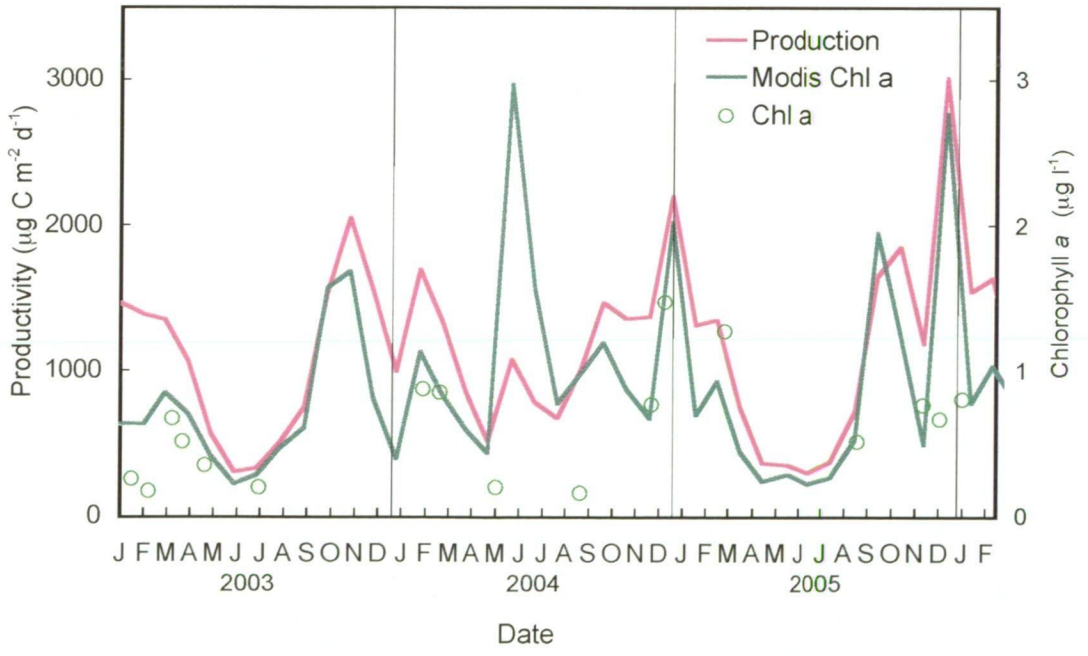

Figure 4.5 *In situ* Chlorophyll *a* concentration 5nm offshore from Couta Rocks (circles), mean monthly Chlorophyll *a* concentration and modeled net primary production from satellite data averaged over coastal waters of NW Tasmania (Box 2)

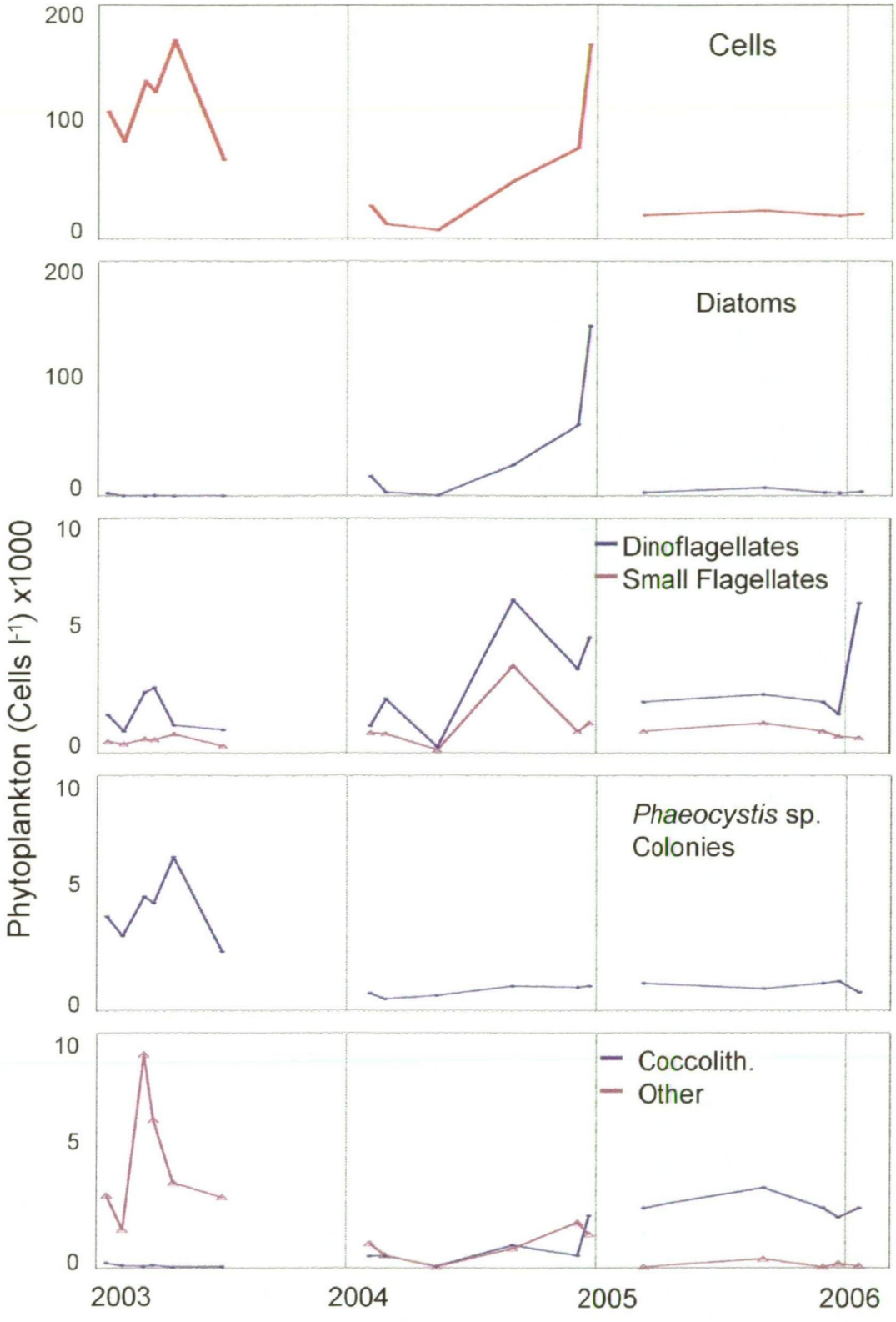

Figure 4.6 Phytoplankton cell counts in seawater from the Couta Rocks field site, please note different y scale for the first two panels. *Phaeocystis* sp. colony number is displayed (colonies between 20-50 cells), 'Other' category includes Chrysophytes, Chlorophytes and unknown cells

4.4.3 Methyl halides

Methyl halide concentrations in seawater and in surface air directly above the sea are shown in Figure 4.7 and 4.8. Saturations are shown in Figure 4.9 values are summarized in Table 4.1.

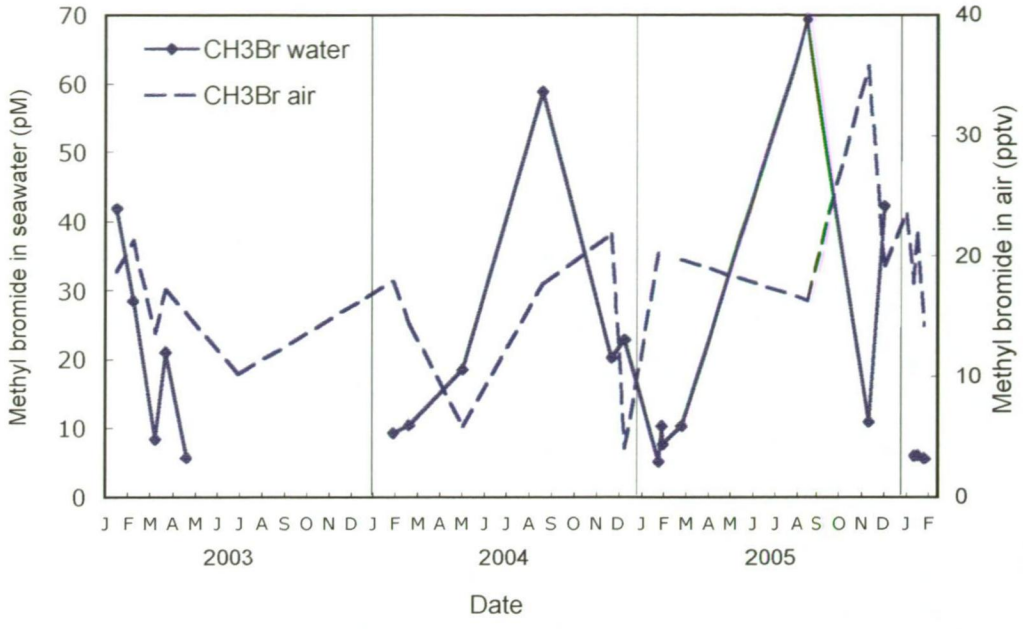

Figure 4.7 Methyl bromide concentration in seawater and surface air measured at a site 9 km offshore from Couta Rocks, combined with measurements at 5 km offshore at Cape Grim (see Chapter 5)

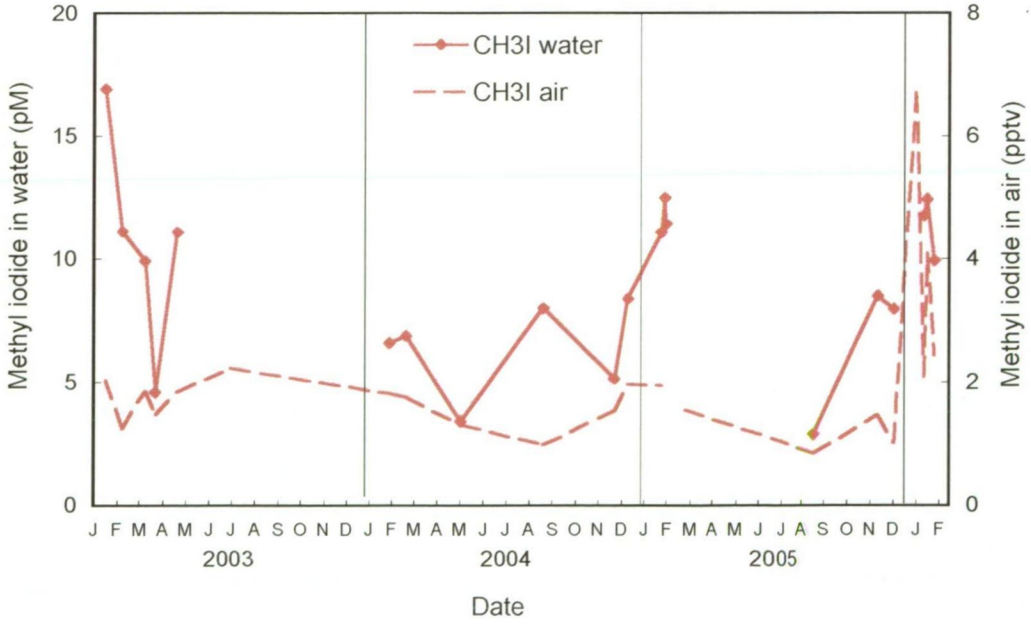

Figure 4.8 Methyl iodide concentration in seawater and surface air measured at a site 9 km offshore from Couta Rocks, combined with measurements at 5 km offshore at Cape Grim (see Chapter 5)

Figure 4.9 Methyl bromide and methyl iodide saturation of surface seawater measured 9 km offshore from Couta Rocks, NW Tasmania

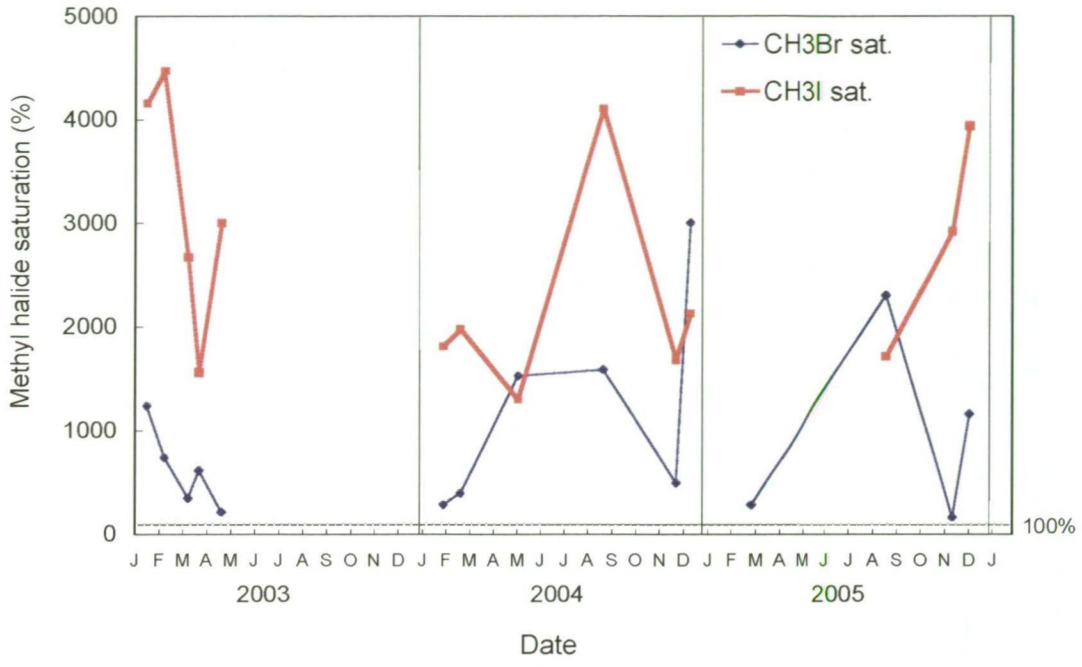

Table 4.1 Methyl halide concentrations in air and water and methyl halide saturation measured 9 km offshore from Couta Rocks, Tasmania

		Average	St Dev	Min	Max
Methyl Bromide	Water (pM)	20	18	5.2	69
	Air (pptv)	9.0	3.5	2.9	17
	Saturation (%)	955	846	161	3006
Methyl iodide	Water (pM)	17	6.5	4.1	36
	Air (pptv)	2.0	1.3	0.8	6.7
	Saturation (%)	2674	1103	1302	4470

4.5 Discussion

4.5.1 Methyl halides

Seawater concentration of methyl bromide was 20 ± 18 pM (range 5 to 69 pM), methyl iodide was 17 ± 6.5 pM (range 4 to 36 pM). These methyl halide concentrations were similar to concentrations measured in other coastal waters elsewhere in the world. Methyl bromide concentration was higher than that measured in coastal seawater off the east coast of England, which was 2 to 3 pM, with a peak of 8.7 pM during bloom conditions (Baker *et al.* 1999). Concentration of methyl iodide was also slightly higher than that measured at 2 to 10 km offshore from Mace Head, which was 9.72 ± 1.9 pM (Carpenter *et al.* 2000). Methyl iodide concentration was within the lower range of that measured in the English Channel, which ranged from 6 to 146 pM (Archer *et al.* 2007). There was a similar pattern of decrease with distance from the shore as was found in other regions such as at Mace Head, Ireland (Carpenter *et al.* 2000, Baker *et al.* 2000). Both methyl iodide and methyl bromide were consistently super-saturated in seawater, indicating that the coastal waters consistently represent a source of these gases. This was found in previous measurements at the same site (Sturrock *et al.* 2003, Corno *et al.* 2004).

Both methyl bromide and methyl iodide concentrations varied considerably over the sampling period. Concentrations of methyl halides can vary over multiple timescales from daily, weekly, seasonal and inter-annual scales. Samples were always taken at the same time of day, avoiding the effect of daily cycles on the measurements. However, sampling was not frequent enough to discern short-term changes of weeks, the main variation observable here are seasonal and inter-annual changes. There is some indication of a seasonal cycle in methyl bromide and methyl iodide seawater concentration, shown using a fitted interpolation spline (degrees of 5 or 6; Figure 4.10). There also appears to be a period of high methyl bromide concentration present in very early spring, repeated in 2004 and 2005.

When fitted to a single sinusoid, the time series is inconsistent with a simple sinusoidal seasonal cycle for either methyl bromide ($R^2 = 0.36$) or methyl iodide ($R^2 = 0.28$). This contrasts with methyl iodide concentration in the English Channel, where there is a strong, simple sinusoidal seasonal cycle of methyl iodide with an

order of magnitude variation by season (Archer *et al.* 2007). However, when fitted with a second component of a fourier sequence, the cycle is more accurately described for both methyl bromide ($R^2 = 0.89$) and methyl iodide ($R^2 = 0.72$). This suggests that there are two or more components to the seasonal cycle of methyl halide concentration. The complex oceanography of the region may contribute to these components. The period of maximum concentration of methyl iodide loosely matches the period of maximum methyl iodide in 'baseline' air at the Cape Grim station (Figure 4.11). This pattern was also present but not strong in the previous measurements made at the same site (Corno *et al.* 2004).

The cycles of methyl halide saturation are similar to that of methyl halide concentration (Figure 4.10), but the fit to a sinusoid with two components of the fourier sequence is poorer (methyl bromide $R^2 = 0.80$, methyl iodide $R^2 = 0.51$). The methyl bromide saturation does not fit the relationship with sea surface temperature outlined in open ocean waters by King *et al.* (2002), ($R^2 < 0.2$).

Part of the reason that the pattern of sea-air saturation is more unpredictable compared to seawater concentration may be that the sampled air is not always from a true marine origin. Since the study site is only 9 km from shore, when wind is blowing offshore the air mass measured may contain input from some terrestrial sources.

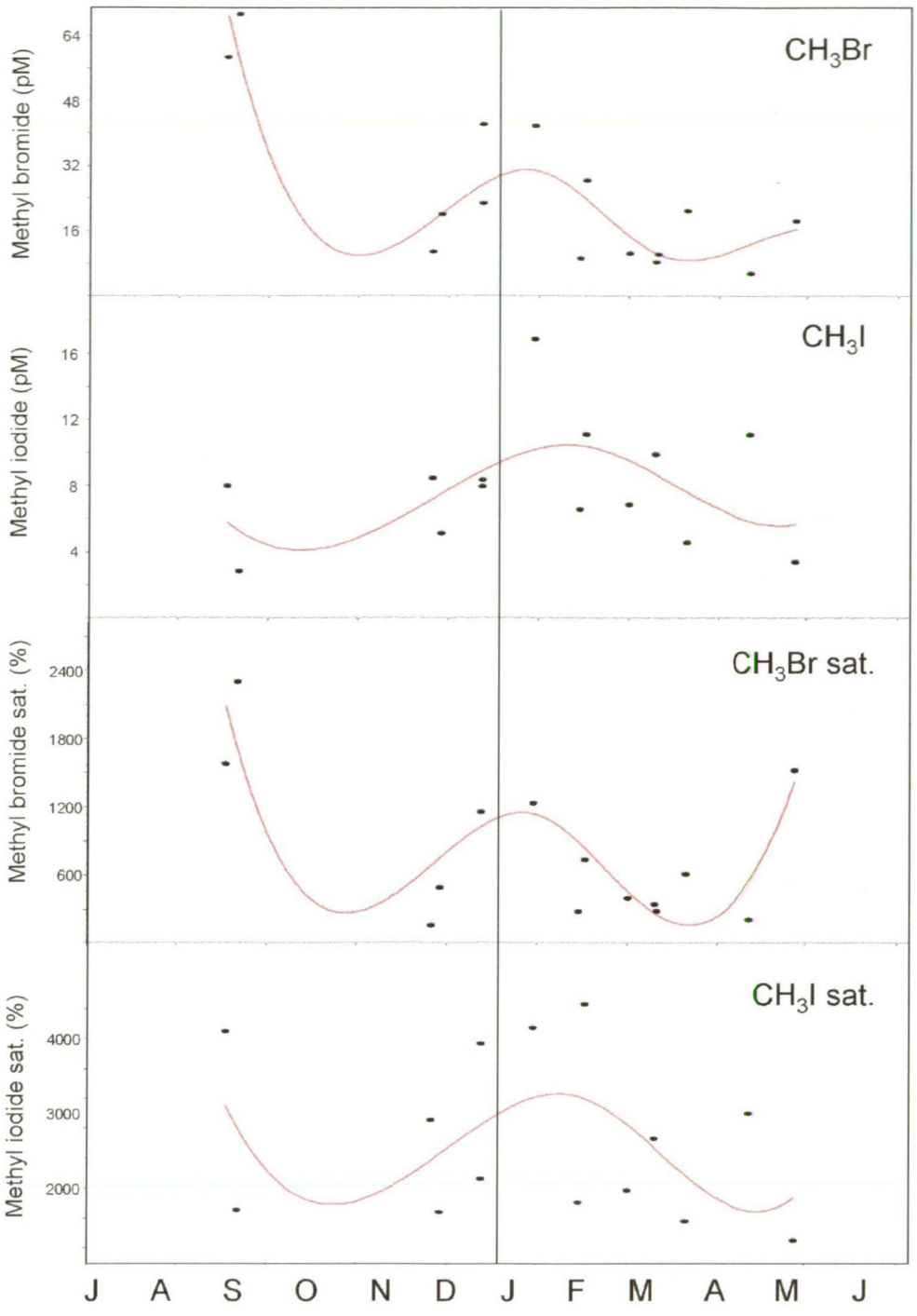

Figure 4.10 Methyl halide concentration and sea-air saturation measured in seawater 9 km offshore from Couta Rocks and 5 km offshore from Cape Grim, NW Tasmania (see Chapter 5), measurements from 2003 to 2006 are shown on a common year scale centred on new year, each plot shows a fitted spline

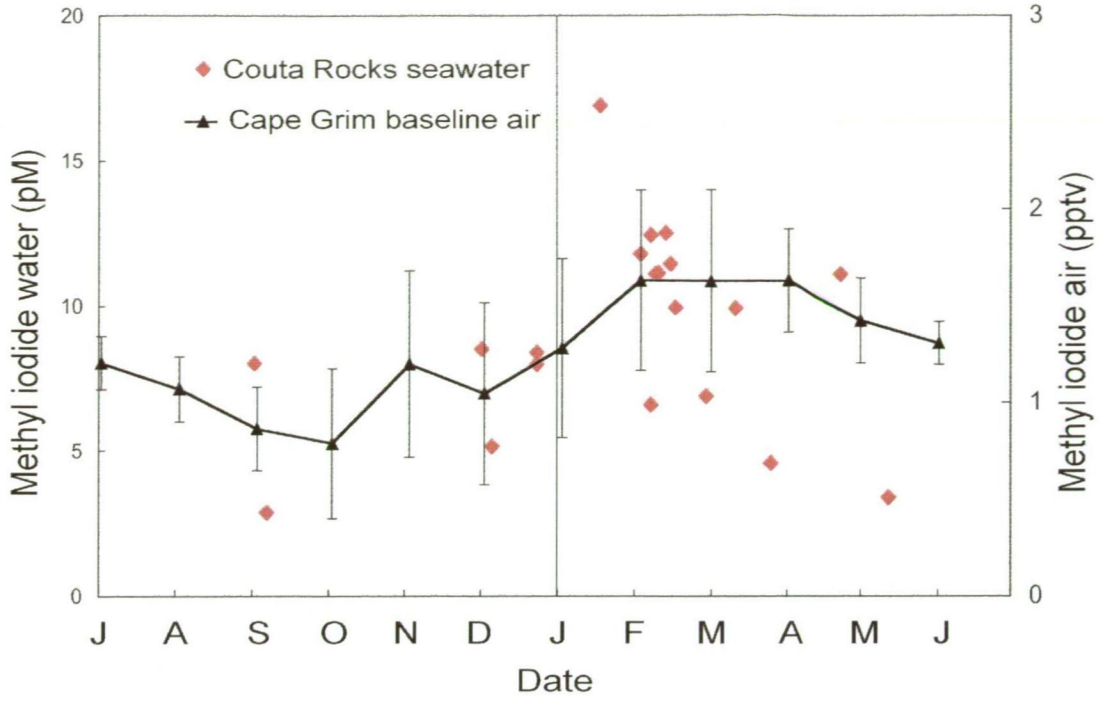

Figure 4.11 Methyl iodide concentration measured in seawater at Couta Rocks, and at 5 km offshore from Cape Grim (see Chapter 5), and the monthly average and standard deviation of methyl iodide in baseline air at Cape Grim

4.5.2 Phytoplankton dynamics and methyl halides

There was no recurring spring bloom or smaller autumn bloom in phytoplankton biomass found in the *in situ* samples or the satellite data (Figure 4.5). There was however, a generally higher concentration of Chlorophyll *a* measured in the *in situ* samples and in satellite measurements of Chlorophyll *a* and modeled net primary production in warmer months compared to the colder months (Figure 4.4, 4.5). There was a generally lower phytoplankton biomass and production in winter, although satellite data indicates that there were peaks in biomass even during these months (winter 2004, Figure 4.5). This lack of a distinct and large seasonal pattern was found in previous samples from the same site (Sturrock *et al.* 2003).

A significant correlation between phytoplankton biomass and methyl halide concentration may not be seen except in high biomass conditions (e.g. Baker *et al.* 1999). This is because there are marine methyl halide sources and sinks other than phytoplankton. Also, methyl halides are secondary metabolites of the cell (Manley

2002), and there may be limited correlation between primary production of the cell and secondary processes. In addition, the biological source is affected by numerous biotic factors such as stress, grazing the stage of growth (see Chapter 1).

There is no clear and consistent correlation between methyl halide concentration and Chlorophyll *a* concentration in the overall set of measurements here. However, there is a concurrent increase in modeled net primary production and methyl halide concentration during December 2004 and November-December 2005 (Figure 4.12).

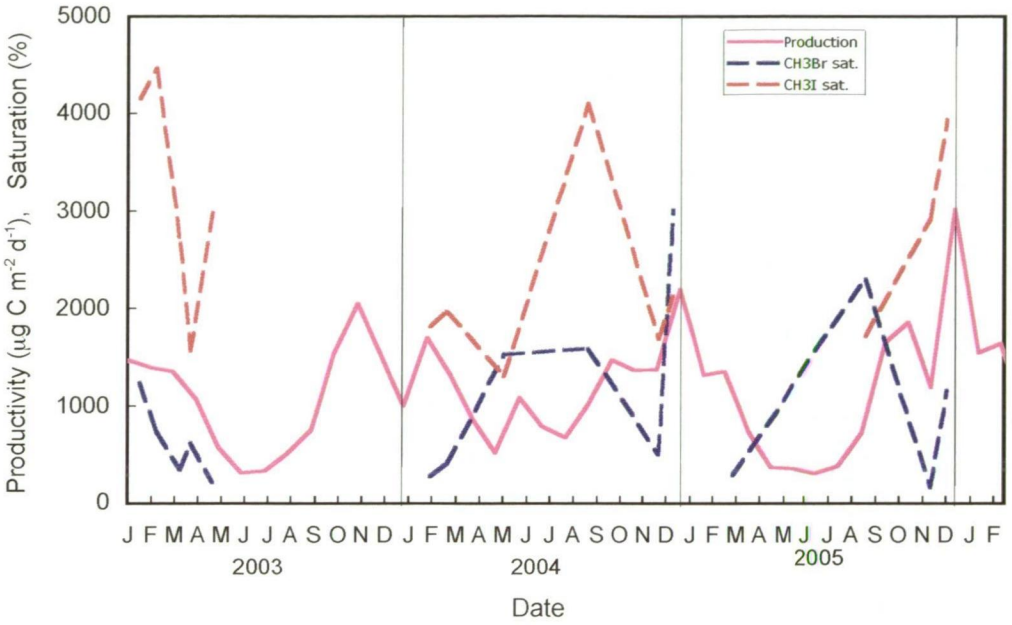

Figure 4.12 Methyl halide saturation measured at 9 km offshore from Couta Rocks, net primary production in the water column modeled from MODIS ocean colour data for northwest Tasmanian waters (Box 2)

Phytoplankton cell counts are notoriously influenced by analyzer experience and two counters rarely obtain the same results. Two different operators conducted the phytoplankton cell counts, Chris Lane (IASOS, University of Tasmania) in 2003 and myself in the later samples. This introduced unavoidable biases between the two datasets, however the trends in each year can be looked at in isolation. In 2003 the phytoplankton community was dominated by *Phaeocystis* sp. colonies and chrysophytes. There was no strong relationship between phytoplankton biomass or cell number of any phytoplankton group and methyl halide concentration in the seawater or methyl halide saturation. There were no strong trends in cell counts of the *in situ* samples and methyl halide concentration during 2005 and 2006.

The most pronounced phytoplankton community changes occurred through the last half of 2004, including a significant bloom of diatoms in December 2004. On 12th May 2004 the waters were extremely clear, with a compensation depth of 60 m (Figure 4.2) and quite low in Chlorophyll *a* (Figure 4.4). On August 31st 2004, there were significant numbers of diatoms of the genus *Thalassiosira* in the water column, as well as dinoflagellates in the genus *Dinophysis* among others, and small flagellates (see Figure 4.5). However the overall phytoplankton biomass, measured as Chlorophyll *a* concentration, was still quite low. On 4th December 2004, the numbers of dinoflagellates, small flagellates and diatoms of the genus *Thalassiosira* had declined, and there were increased numbers of diatoms of the genus *Chaetoceros*. A significant increase in diatom cell number occurred between 4th and 22nd December 2004, dominated by the genus *Chaetoceros*. On this day the average cell count for 0 to 20 m was 140,000 cells l^{-1}, with a sub-surface maximum of 340,000 cells l^{-1} at 10 m depth. A drop in nutrients accompanied this bloom, particularly nitrogen and silica, as shown in Figure 4.13. The bloom was also accompanied by a rise in methyl bromide and methyl iodide concentration between these two dates (Figure 4.14), and also in saturation. Saturation is affected by the concentration in both the water and the air, and the air concentration may be affected by sources from further away. Therefore, although the saturation appears to increase significantly, this may not be a reliable indicator of an increase in the marine source. So over this period, methyl halide saturation appears to be partially correlated to phytoplankton biomass, especially the flagellates, followed by some evidence of an increase in concentration during the bloom of diatoms (Figure 4.14).

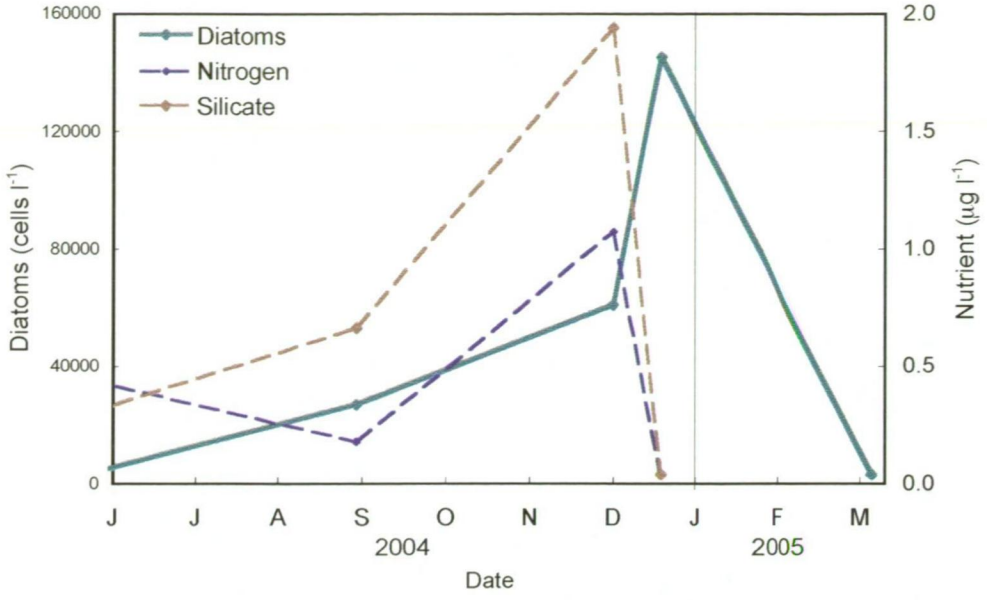

Figure 4.13 Total nitrogen (nitrate and nitrite) and silica concentrations and diatom cell number in Couta Rocks coastal seawater, 2004-05

The correlations between diatom and dinoflagellate biomass and methyl halide concentration and saturation are not significant (R^2 <0.71). Since the effects of the various phytoplankton groups, as well as the other source and sink terms that contribute to the overall saturation of methyl halides are also present, a significant correlation of confidence >0.9 was not expected. Therefore, these indicative relationships are reasonably good evidence for a biological source of methyl halides from phytoplankton during this high biomass event. Various dinoflagellates have been shown to produce methyl halides in incubation studies (see Table 1.3). Also, *Chaetoceros* species of diatoms have been measured to produce methyl bromide in culture, including *Chaetoceros diversum, Chaetoceros atlanticus*, *Chaetoceros calcitrans* (Saemundsdottir & Matrai 1998, Scarratt & Moore 1998, see Table 1.3).

A previous study found that an elevated level of methyl bromide concentration during a coastal bloom of *Phaeocystis* sp. (Baker *et al.* 1999). A similar increase was found in previous data obtained at the Couta Rocks site, when an eight-fold increase of Chlorophyll *a*, was accompanied by a five-fold increase in methyl bromide concentration in seawater between February and March 2001 (Corno *et al.* 2004).

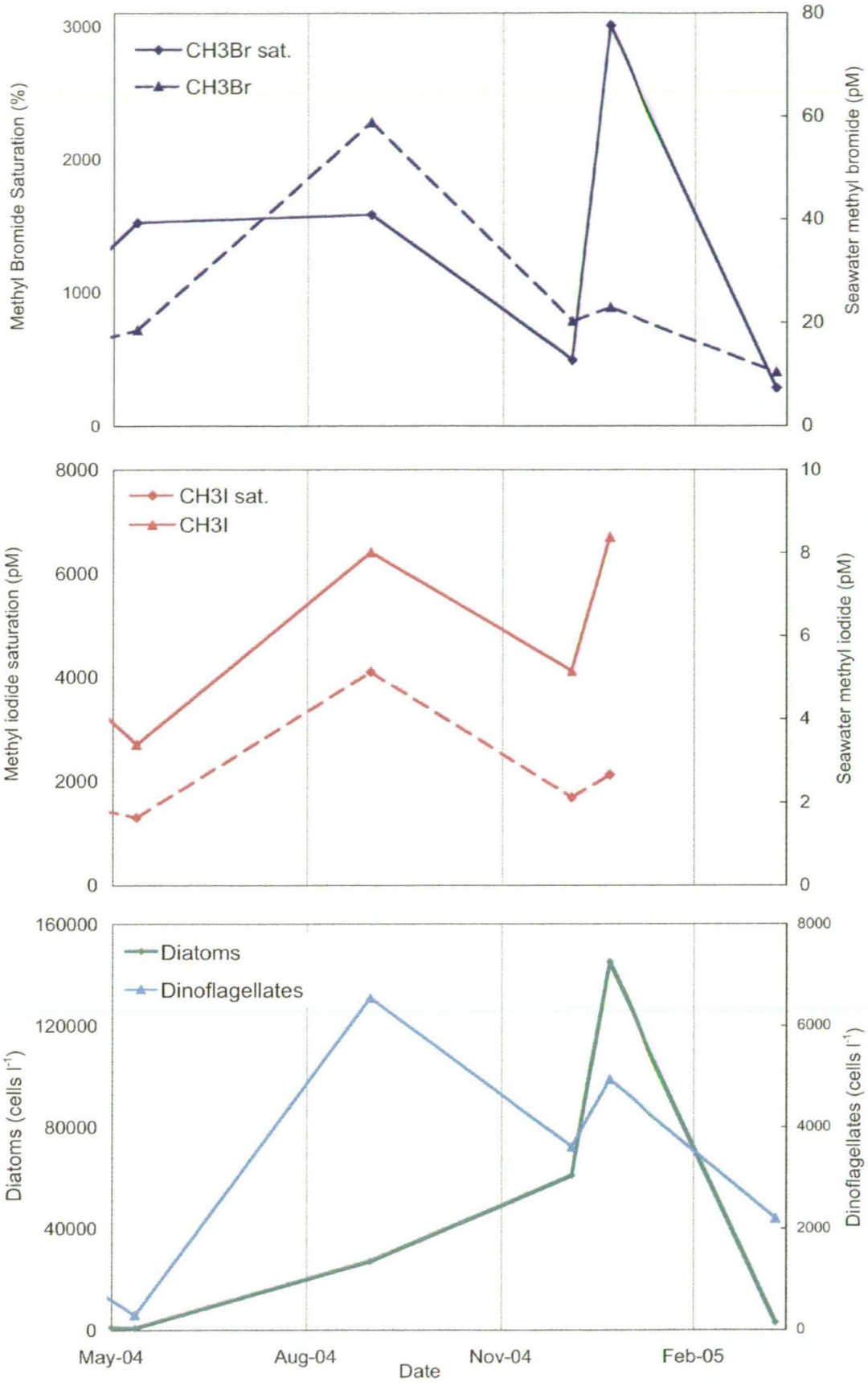

Figure 4.14 Methyl bromide and methyl iodide saturation, diatom and dinoflagellates cell number in Couta Rocks coastal seawater, 2004-05

4.5.3 Other correlations

Over seven measurements during the summer months of 2000-2001, Corno *et al.* (2004) found significant correlations between methyl bromide and N:P ratio (R^2 = 0.92), as well as an indicative inverse relationship between methyl iodide concentration and low nitrate conditions (R^2 = 0.70). This trend is not as strong in this later data. There were relationships between nutrients and methyl halide concentration, notably an inverse relationship over the bloom period in 2004 between methyl bromide saturation to silica and nitrate + nitrite (n = 4, R^2 = 0.80 & 0.93 respectively). An inverse relationship between nitrate + nitrite and methyl iodide concentration in seawater exists over late 2004 and 2005 (n = 6, R^2 = 0.97). There is an indicative relationship between N:P ratio and methyl iodide concentration in the data from 2003 and early 2004 (n = 5, R^2 = 0.82), but this relationship was weaker throughout the rest of the sampling period. Methyl bromide had only a weak inverse correlation to N:P in the early months of 2004 (n = 4, R^2 = 0.80) and nowhere else. These correlations are not considered reliable since the number of points is low and the measurements were widely spaced in time.

In the same seven measurements over summer 2000-2001, Corno *et al.* (2004) also found a significant positive relationship between Chlorophyll *a* and methyl iodide (R^2 = 0.92), and a weak relationship to methyl bromide (R^2 = 0.62). This relationship is not confirmed by these subsequent measurements. The greatest correlation with Chlorophyll *a* was a negative relationship with methyl bromide saturation over February to December 2004 (n = 5, R^2 = 0.99), and the subsequent positive relationship with diatom abundance over the bloom mentioned above.

However, looking for the correlation of these variables is problematic for two reasons. First the sampling was too infrequent to capture all scales of variability. Oceanographic, photochemical and phytoplankton processes occur on scales of hours, days to weeks. Changes to methyl halide concentrations, due to physical processes and biological production in coastal waters can vary quite considerably from week to week, as evidenced by the measurements in Archer *et al.* (2007). The frequency of sampling outlined in Corno *et al.* (2004) and Sturrock *et al.* (2003) was higher, including seven field trips over one summer. Short-term temporal changes of the biological source of methyl halides are more likely to result in meaningful

correlations between these variables, however the ideal sampling regime would be far more frequent than this, with measurements made daily or even hourly. Only broad-scale seasonal and inter-annual trends are observable in the data presented here.

The second reason that looking for correlations is problematic is that the concentration and saturation of methyl halides is the net result of all the different processes occurring at these different timescales, with various cause and effect mechanisms present. Therefore, a correlation to any one variable taken in isolation would be rare and may not provide evidence of a causal link. An example is a correlation to nutrient concentration. Previously it was suggested that a correlation between low nitrogen conditions and methyl halide concentration is evidence that the methyl halide production is a response to nutrient depletion (Corno *et al.* 2004). This may be misleading in the case of a coastal phytoplankton bloom (see Figure 4.13 & 4.14), where heightened biological activity may partially contribute to an increase in methyl halide concentration and also result in nutrient depletion. The bloom of diatoms caused a depletion of nutrients and a slight increase in methyl bromide concentration, rather than the depletion of nutrients causing the diatoms to produce more methyl bromide. Considering all indicators of bloom conditions, including increased phytoplankton biomass and nutrient depletion, may give some indication that there may be enhanced methyl halide production.

4.6 Conclusions

The region of coastal waters off northwest Tasmania were consistently supersaturated in methyl bromide and methyl iodide, and were therefore always a source of these gases to the atmosphere. The concentration of methyl halides in seawater varies considerably over annual and inter-annual timescales, however the seasonal cycle is not adequately decribed by a single sinusoid. There was no consistent seasonal cycle of phytoplankton abundance or community structure, however there were a few incidents of elevated biomass and succession of species. There was no consistent clear correlation between the concentration of methyl iodide or methyl bromide and phytoplankton, except for a series of events in late 2004,

including a bloom of diatoms of the genus *Chaetoceros* concurrent with and a slight increase in the concentration of methyl bromide. A link between the numbers of flagellates and the concntration of methyl iodide was also indicated during the period.

The controlling factors on the biological source of methyl halides in these waters can't be isolated due to the infrequency of sampling and the complexity of the production mechanisms. However, generally speaking there appears to be a consistent saturation of both methyl halides, with high variability and episodic elevated saturation of one or the other methyl halide related to high biomass bloom of a phytoplankton species.

Chapter 5. Production of methyl halides in inshore waters less than 5km offshore at Cape Grim

5.1 Introduction

This chapter focuses on the production and emission of methyl halides at the coast and in waters less than 5 km offshore in northwest Tasmania, where the effect of macroalgae is likely to be significant. Measurements of the concentration of methyl bromide and methyl iodide in the inshore and coastal waters near Cape Grim are presented, along with measurements of kelp biomass at the coast and on the beach. The effect of intense emissions at the coast may be detected as peaks in concentration measured at Cape Grim station, and may have effects on the atmospheric chemistry unique to the coastal margin, which is discussed in Chapter 6.

Of specific interest here is the presence of any 'enrichment' of methyl halide concentration in or near kelp beds compared to further offshore, and the spatial pattern of methyl halide concentration with distance from shore.

5.2 Methods

Samples of surface waters were taken under two sampling strategies: daily temporal profiles and spatial transects. Daily profiles were made at Valley Bay in 2006 and Stanley wharf in 2005, transects were completed directly adjacent to Cape Grim in 2005 and 2006. A survey of biomass of living kelp on the reef at Cape Grim and beach-cast kelp on the adjacent beach was also performed.

5.2.1 Site Description

Cape Grim faces directly into the open Southern Ocean, the coast is exposed with frequent strong winds and high wave action. The town of Stanley lies around the northwest tip of the Tasmanian mainland and faces onto the less exposed Bass Strait, but is still subject to relatively high wave action and strong winds. Stanley is in a

region of higher tidal range and earlier tidal cycle (one hour before Cape Grim, see Chapter 2).

There are rocky reefs adjacent to both sites. Exposed temperate rocky reefs in this region support a diverse variety of macroalgae, fish and invertebrates. They contain a variety of sub-tidal macroalgae, including species from the Divisions Rhodophyta (red algae) and Chlorophyta (green algae) but the largest biomass is represented by the Phaeophyta (brown algae). These include *Phyllospora comosa* (crayweed), *Ecklonia radiata, Crystophora* spp., *Sargassum* spp. and *Macrocystis pyrifera* (giant kelp). However the intertidal zone is dominated by a single brown algal species: bull kelp (*Durvillaea potatorum*). This species is the focus of this study, since it will be responsible for direct emissions to the atmosphere and the only species subject to photo-oxidative stress at low tide, which can initiate halocarbon emission (Pedersen *et al.* 1996). Various species of beach-cast kelp are present on the sandy beach adjacent to Cape Grim (Valley Bay), including giant kelp, crayweed and others. However bull kelp makes up most of the biomass. Beach-cast kelp biomass is variable throughout the year, depending on storm surges and wave action.

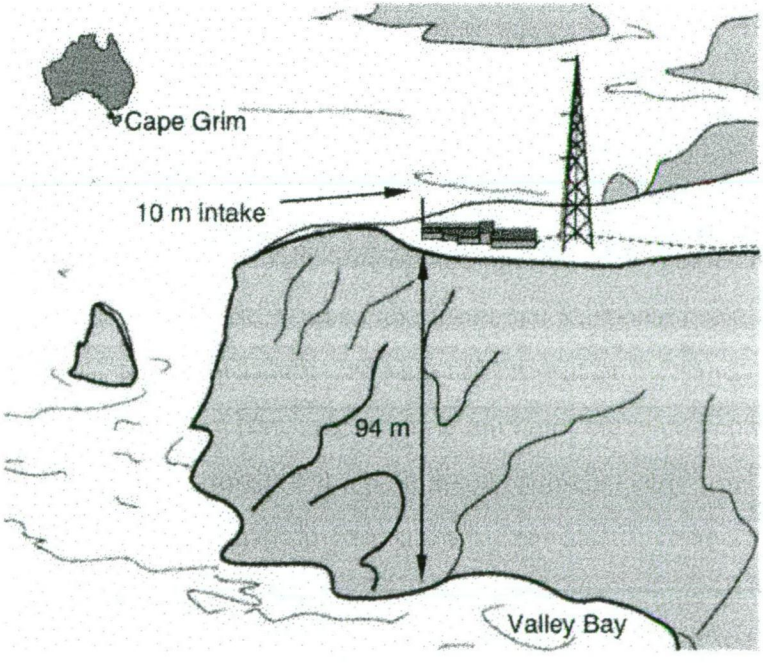

Figure 5.1 Schematic diagram of the northern edge of Valley Bay at Cape Grim, showing position of CG-BAPS and the cliff in front of the station (source: Cainey *et al.* 2007b)

5.2.2 Daily profiles

Three day long profiles of methyl halide concentration in surface waters were made at Stanley wharf (Figure 5.2, 5.3) in 2005. Measurements were made at approximately four hourly intervals over two complete 24 hour periods (2nd, 9th February) and one other day from dawn until after dusk (5th February). Water samples were collected using a bucket. One air sample was taken on the 2nd February and two samples were taken on the 9th February in an evacuated, glass lined, stainless steel flask (see Chapter 4 for method).

In 2006, four days of measurements were made at the northern end of Valley Bay beach adjacent to the Cape Grim station at the bottom of the 94 m cliff (Figure 5.4). Seawater samples were taken at two-hour intervals from 6 am to 8 pm and another sample at 9pm, which covered the period dawn until dusk. Seawater was collected from 30 m offshore among the kelp beds using a moored polypropylene pipe and diaphragm hand pump. Two air samples per day were taken.

Tide data for Stanley was obtained from the National Tide Centre from the gauge on Stanley wharf and tide at Cape Grim was calculated using an offset to the Stanley gauge (see Chapter 2). Light data was obtained from the Cape Grim radiation program (Dr Stephen Wilson, University of Wollongong). At each sampling time measurements of water and air temperature were made. Water samples were also analyzed for Chlorophyll *a*, phytoplankton cell counts, nutrients, and methyl halide concentration by GC-ECD, details of analysis procedures are outlined in Chapter 4.

To statistically analyze the relationship between tide height, light intensity and the methyl halide concentration in the seawater among kelp beds, two techniques were used: a linear model and an additive model. Where a linear model represents $y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3$ etc, an additive model represents $y = f_1(x_1) + f_2(x_2) + f_3(x_3)$ etc, where f_i are arbitrary smooth transformations of x_i. For a linear model the aim is to estimate the unknown coefficients β_0, β_1 etc, while in an additive model the aim is to estimate the unknown transformation f_i (Hastle & Tibshirani 1990).

Figure 5.2 Photograph showing the Stanley wharf, NW Tasmania

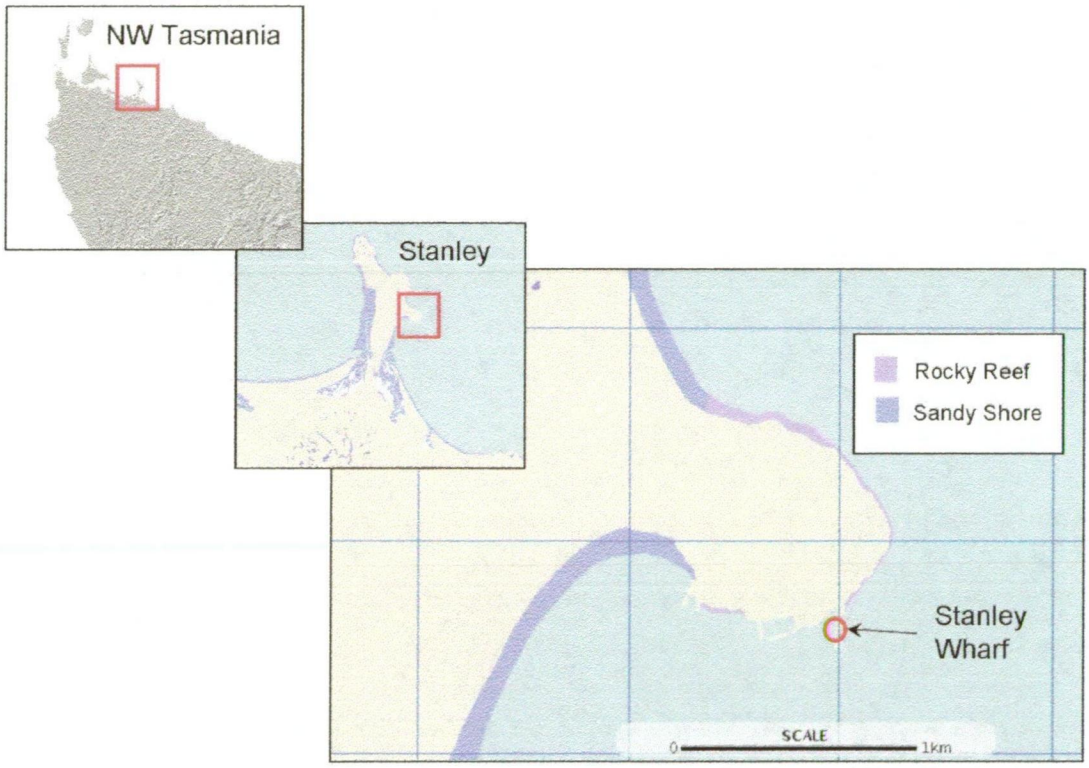

Figure 5.3 Map showing sampling site for daily profile sampling in February 2005, Stanley wharf, NW Tasmania (source: Google maps)

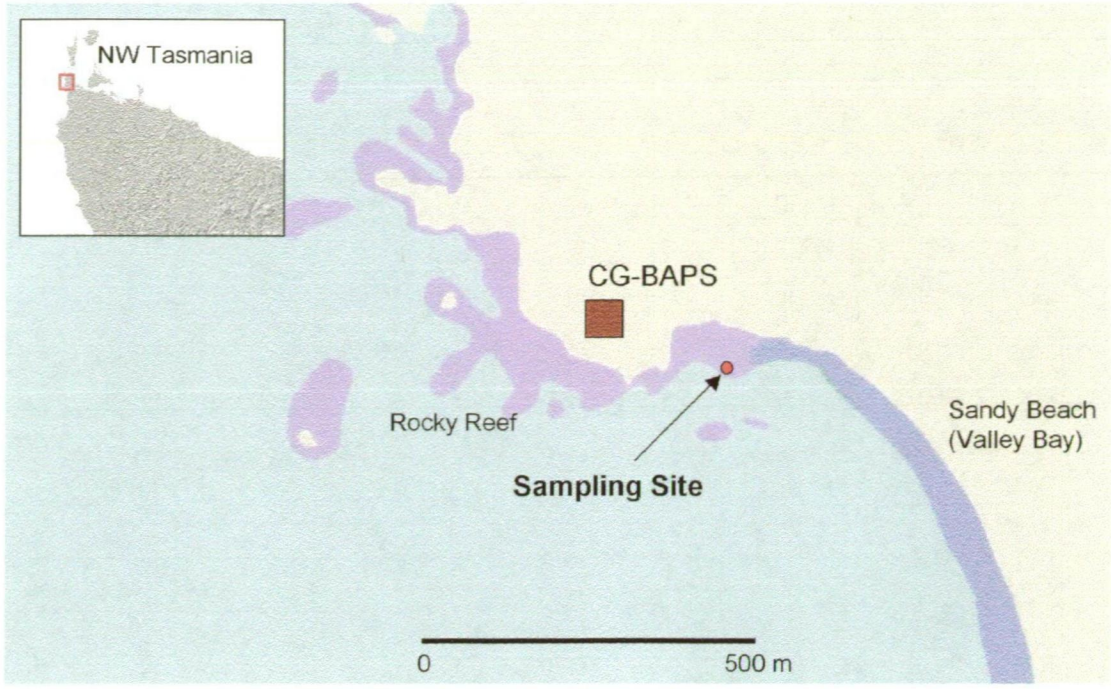

Figure 5.4 Map showing sampling site for daily profile sampling in February 2006, Valley Bay NW Tasmania (source: Google maps)

5.2.3 Transects

In February 2005 and 2006, three transects were made directly offshore from Cape Grim due west to a distance of 5 km, with stations at 0.1, 1, 2 and 5 kilometres from the coast (Figure 5.5). All transects were conducted when a boat was available and weather conditions were suitable for the boat to launch (less than 2 m swell and 10 knots wind) and between the hours of 8:30 – 11:00 am. In 2005, the first two transects were made during a rising tide, the third was during a receding tide. In 2006 the first transect was made during low tide, the second during a receding tide, and the third during a rising tide. Observations of sea, swell, tide, wind, weather water and air temperature were made at all sampling sites, and samples of air, seawater and phytoplankton were taken. Water and air samples were taken at each site and analysed using the same procedure as the Couta Rocks site (see Chapter 4).

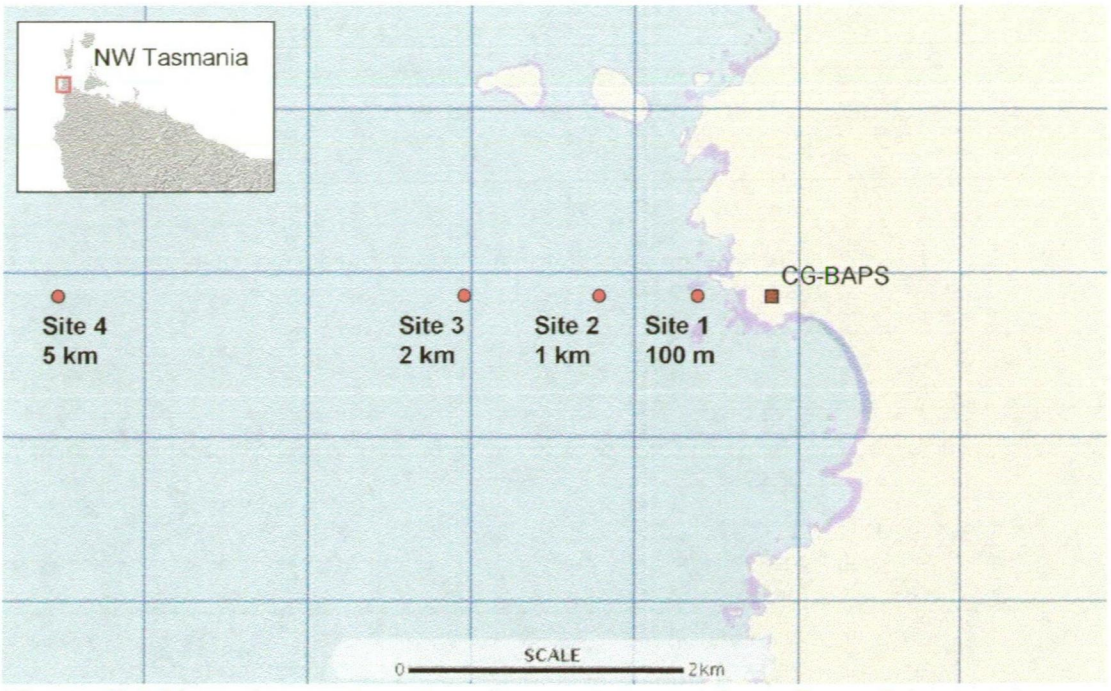

Figure 5.5 Map of sampling sites along a transect from Cape Grim to 5 km offshore made in February 2005 & February 2006 (source: Google maps)

5.2.4 Kelp survey

The density and biomass of bull kelp on the rocky reef immediately in front of Cape Grim station was surveyed in February 2006. 80 plants over a 14 m length of reef were collected and weighed. Plant density was recorded in 22 1 x 1 m quadrats at random sites on the reef.

A stratified survey of beach-cast kelp biomass was performed on a randomly chosen day in April 2006. The beach was divided into two regions for the survey (Figure 5.6), based on visual observation of biomass. Within the high biomass region, kelp biomass was recorded in ten randomly placed 1 x 1 m quadrats. Within the low biomass region, clumps of beach-cast kelp were systematically counted and weighed in 3 sections of beach of 10 metres width, from the water edge to the start of the land vegetation.

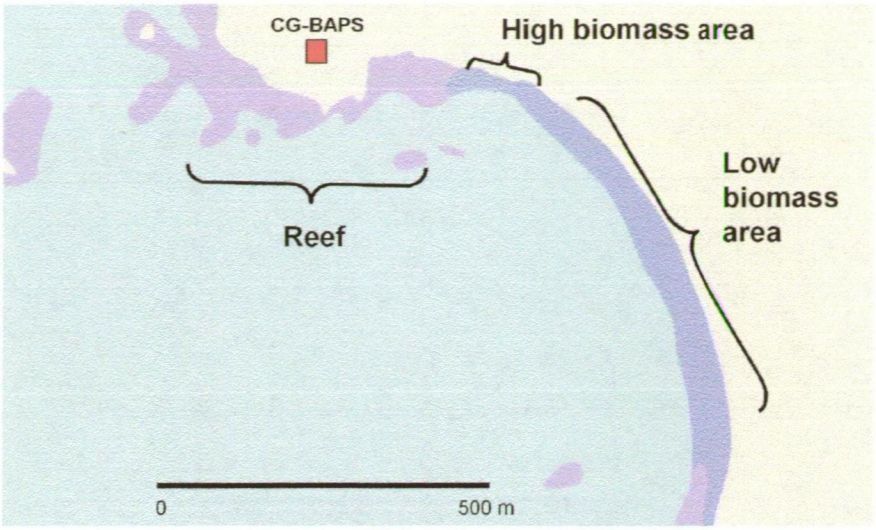

Figure 5.6 Map of Valley Bay beach, northwest Tasmania showing approximate size a position of zones for a survey of beach-cast kelp biomass and rocky reef (Source: Google maps)

5.3 Results

5.3.1 Daily profiles

Measurements from two profiles over 24 hours at Stanley wharf in 2005 are shown in Figure 5.7 and 5.8 and measurements from the profile over 15 hours are shown in Figure 5.9. Methyl bromide concentration in seawater was 25.5 ± 14.1 pM (range 9.1 to 63.5 pM) and methyl iodide concentration in seawater was 13.3 ± 4.8 pM (range 6.0 to 27.4 pM). In three air samples (one on 2/2/05, two on 9/2/05) methyl bromide concentration was 24.5 ± 2.9 pptv, and methyl iodide was 1.04 ± 0.13 pptv. The concentrations of methyl bromide seem extraordinarily high, and may be in error.

Measurements from the four profiles made at Valley Bay in 2006 are shown in Figure 5.10-5.13. Methyl bromide concentration in seawater was 29.7 ± 9.7 pM (range 12.2 to 44.2 pM) and methyl iodide was 28.6 ± 13 pM (range 14.8 to 57.7 pM), except for the afternoon of 11th Feb, when it was above 63.3 pM, peaking at 144.5 pM at 4:00 pm (Figure 5.12). Methyl bromide concentration in air directly above the sea was 2.9 ± 1.5 pptv (range 1.8 to 5.8 pptv) and methyl iodide was 2.7 ± 0.6 pptv (range 2.1 to 3.8 pptv), except for 11th Feb where it was 4.5 pptv in the morning and 5.5 pptv in the afternoon (Figure 5.12). Measurements at the station did not show a similar peak at this time. Air mass origin on the 11th February 2006 was from the baseline sector of the Cape Grim, shown by a back trajectory (Figure 5.14).

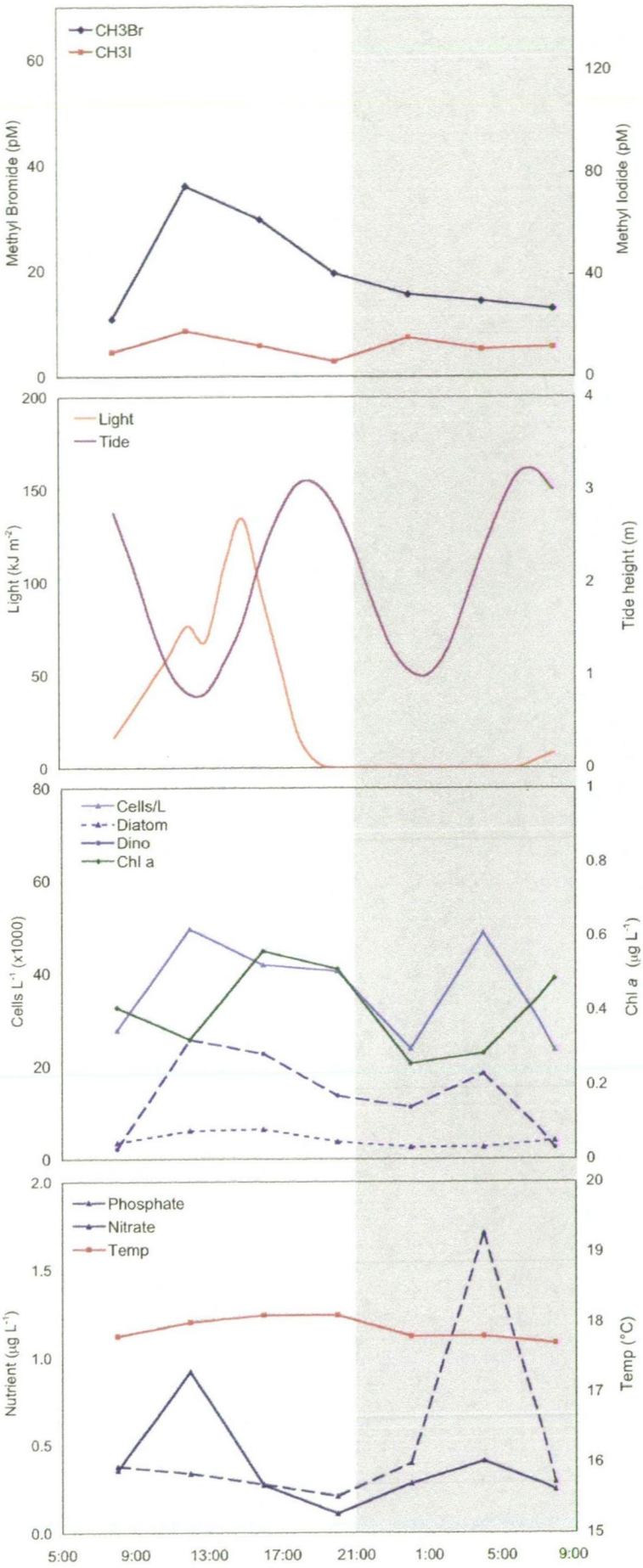

Figure 5.7 Measurements of methyl halides and surface seawater properties over 24 hours made at Stanley wharf, 2-3 Feb 2005

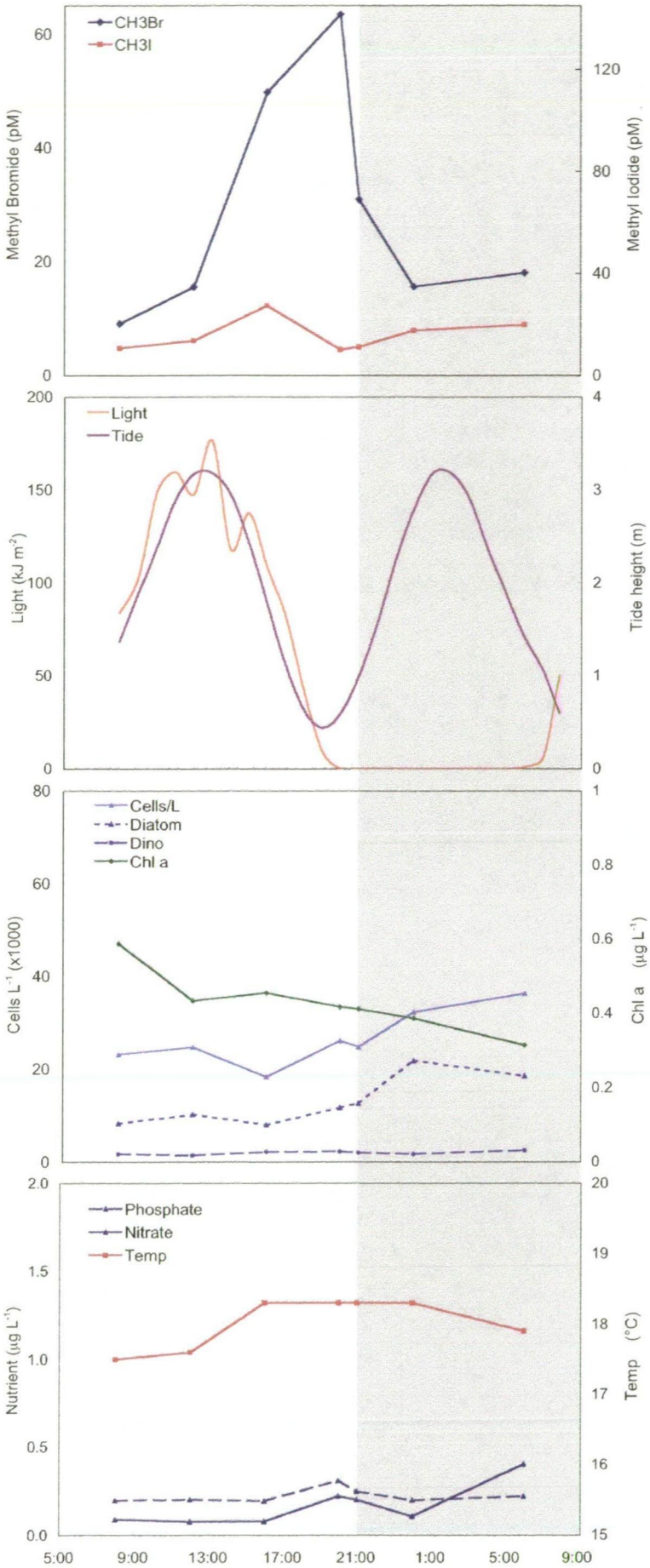

Figure 5.8 Measurements of methyl halides and surface seawater properties over 24 hours made at Stanley wharf, 9-10 Feb 2005

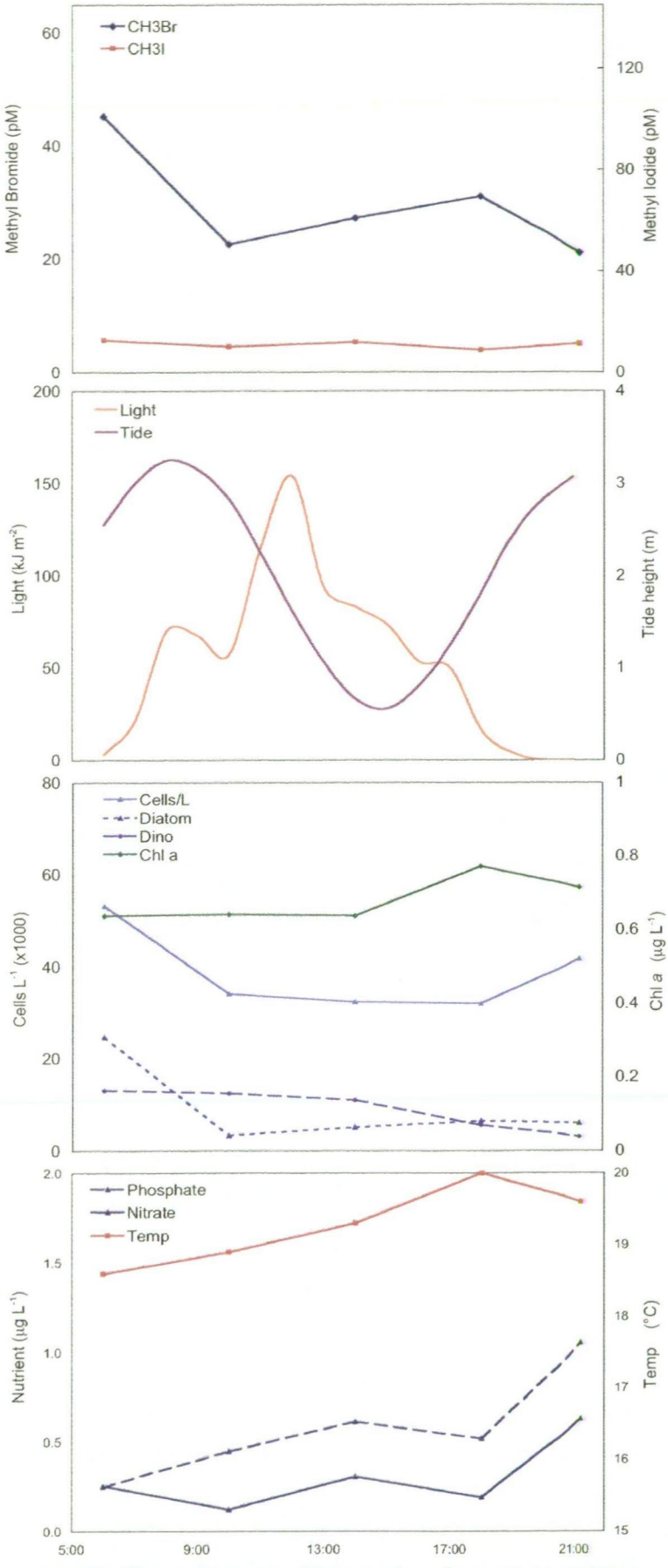

Figure 5.9 Measurements of methyl halides and surface seawater properties over 15 hours (dawn until dusk) at Stanley wharf, 9-10 Feb 2005

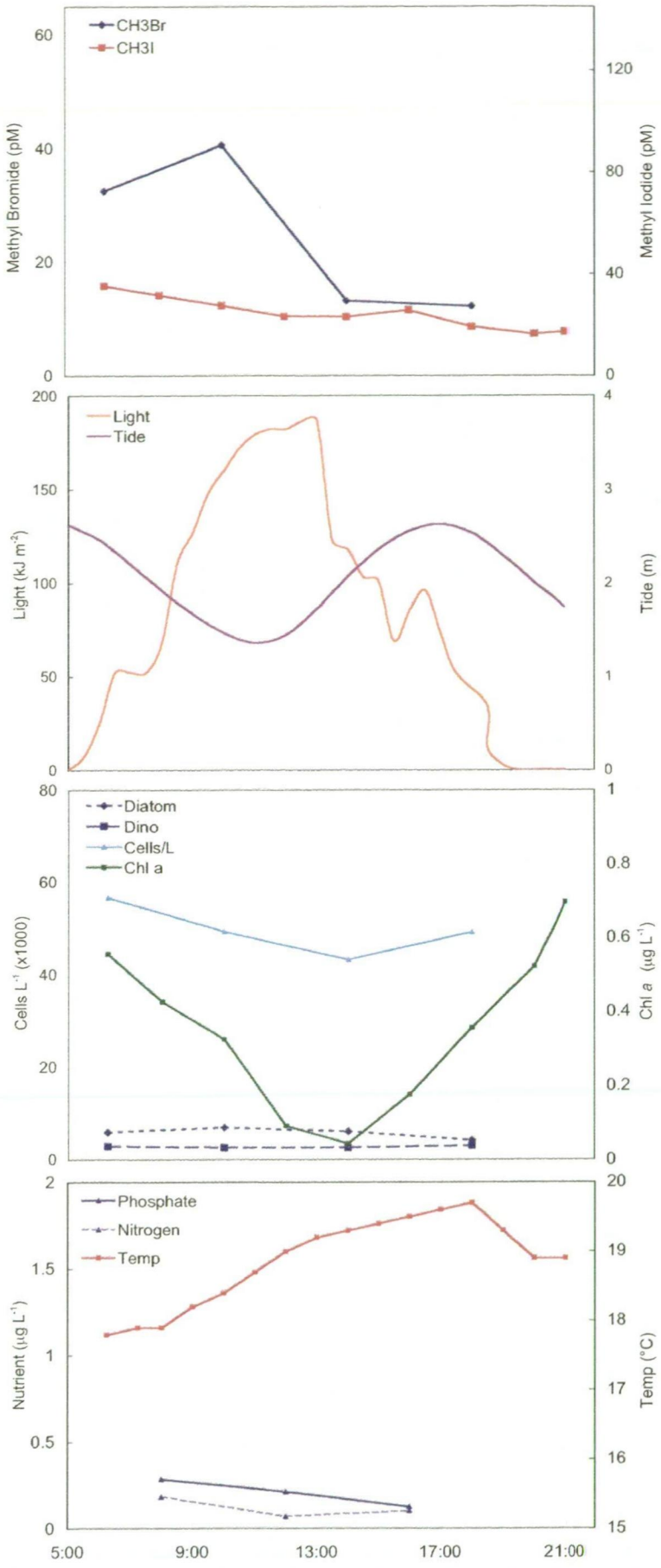

Figure 5.10 Measurements of methyl halides and surface seawater properties over 15 hours (dawn until dusk) at Valley Bay, 3rd February 2006

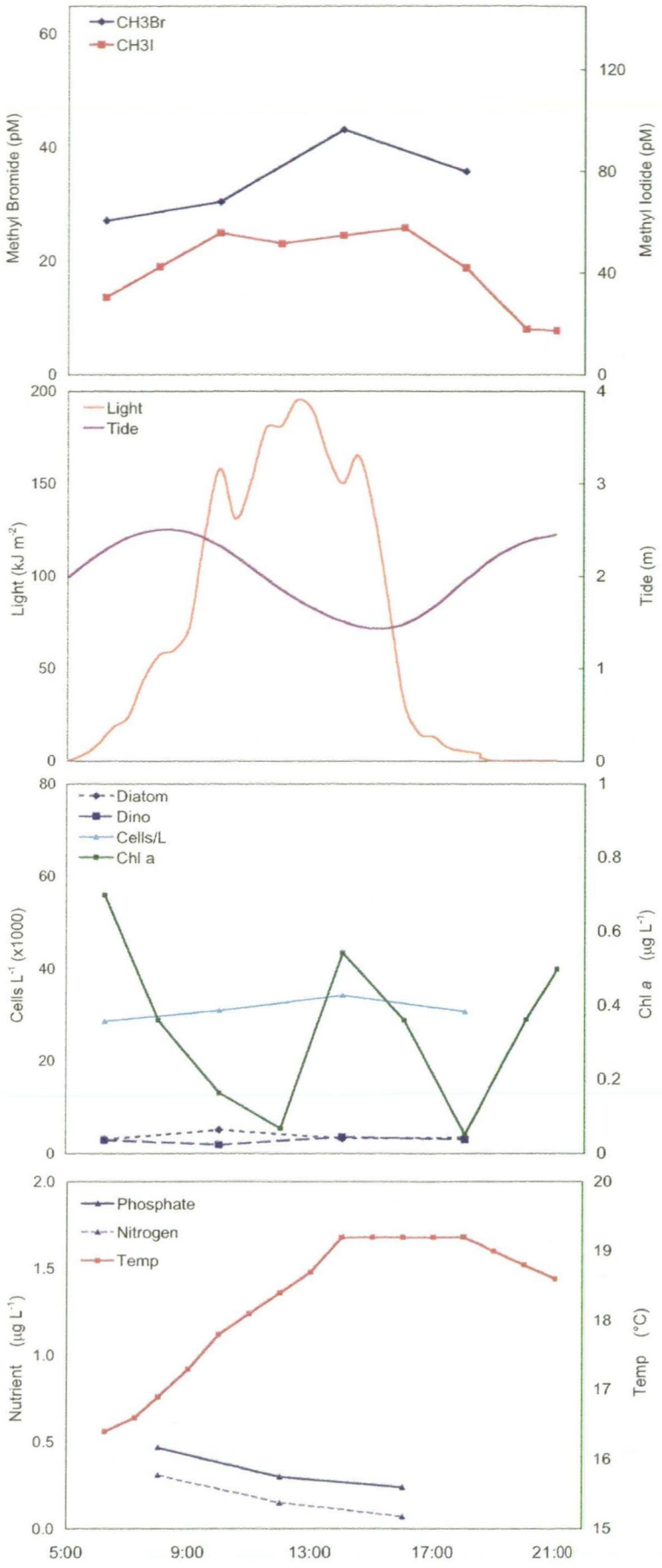

Figure 5.11 Measurements of surface seawater properties over 15 hours (dawn until dusk) at Valley Bay, 8th February 2006

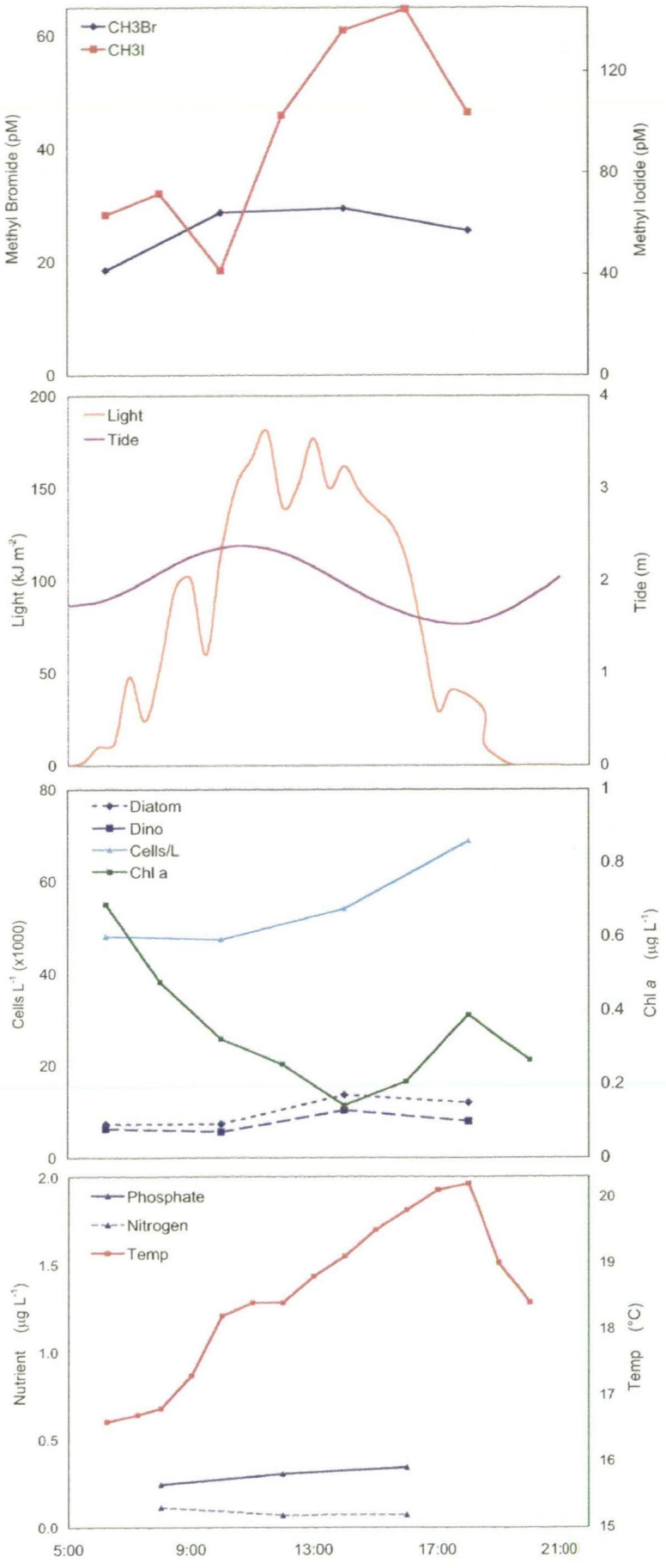

Figure 5.12 Measurements of surface seawater properties over 15 hours (dawn until dusk) at Valley Bay, 11th February 2006

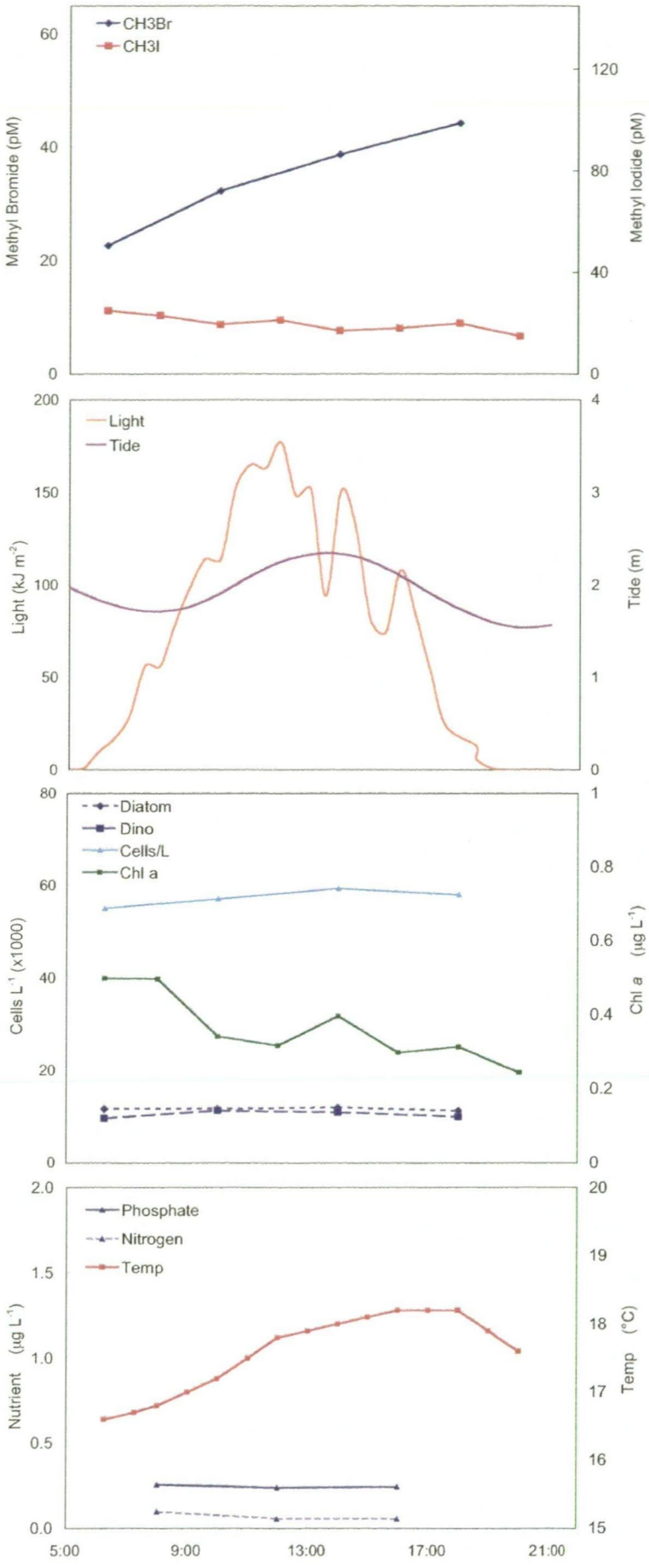

Figure 5.13 Measurements of surface seawater properties over 15 hours (dawn until dusk) at Valley Bay, 14th February 2006

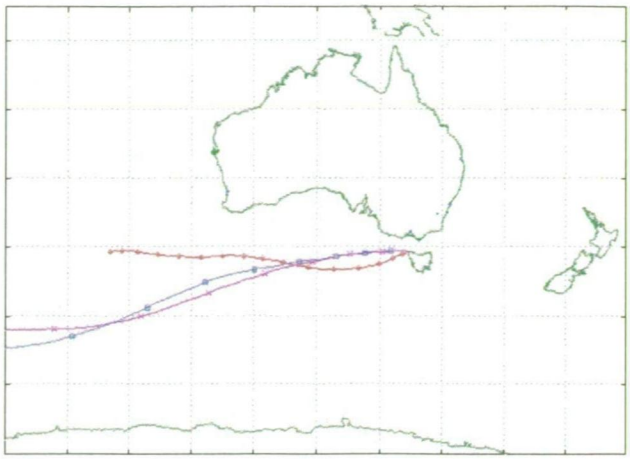

Figure 5.14 Air mass back trajectory of air arriving at Cape Grim on the afternoon of 11th February 2006, data points are every 6 h back to 96 h at three air pressures (red 1000 hPa, blue 700 hPa, purple 550 hPa)

5.3.2 Transects

Data from transects in 2005 are presented in Figures 5.15, data from transects in 2006 are presented in Figures 5.16. Average values for the Valley Bay daily profiles are included in the 2006 figures for reference. Methyl iodide and methyl bromide concentrations in seawater were highest near the rocky reef, with a rapid decrease moving away from the coast measured in each transect in both years. The pattern is consistent with a log relationship (Figure 5.17). In 2005, methyl iodide decreased to 11.7 ± 0.73 pM (range 11.1 to 12.5 pM), and methyl bromide down to 7.7 ± 2.6 pM (range 5.2 to 10.4 pM) at 5 km offshore. In 2006, methyl iodide decreased down to a level of 11.4 ± 1.3 pM (range 9.9 to 12.4 pM), and methyl bromide down to 5.9 ± 0.3 pM (range 5.6 to 6.12 pM) at the 5 km site.

Phytoplankton biomass as measured by Chlorophyll *a* was generally lower and more variable nearer the coast. At 5 km from the coast, Chlorophyll *a* was 0.7 ± 0.07 μg L^{-1} in 2005 and 0.6 ± 0.08 μg L^{-1} in 2006. Chlorophyll *a* was lowest and most variable at the inshore location examined in 2006 (0.33 ± 0.17 μg L^{-1}). The phytoplankton community contained diatoms, dinoflagellates, chlorophytes, coccolithophorids and *Phaeocystis* sp. colonies, with no consistent pattern with distance from shore. Inshore waters were depleted in nitrogen compared to offshore waters. In 2006, total nitrogen was 0.59 ± 0.1 μM at all sites >100 m, and was 0.11 ± 0.07 μM near the shore (Figure 5.9). Phosphorous was not similarly depleted, resulting in a N:P ratio of 0.4 ± 0.2 inshore and 2.0 ± 0.5 offshore in 2006.

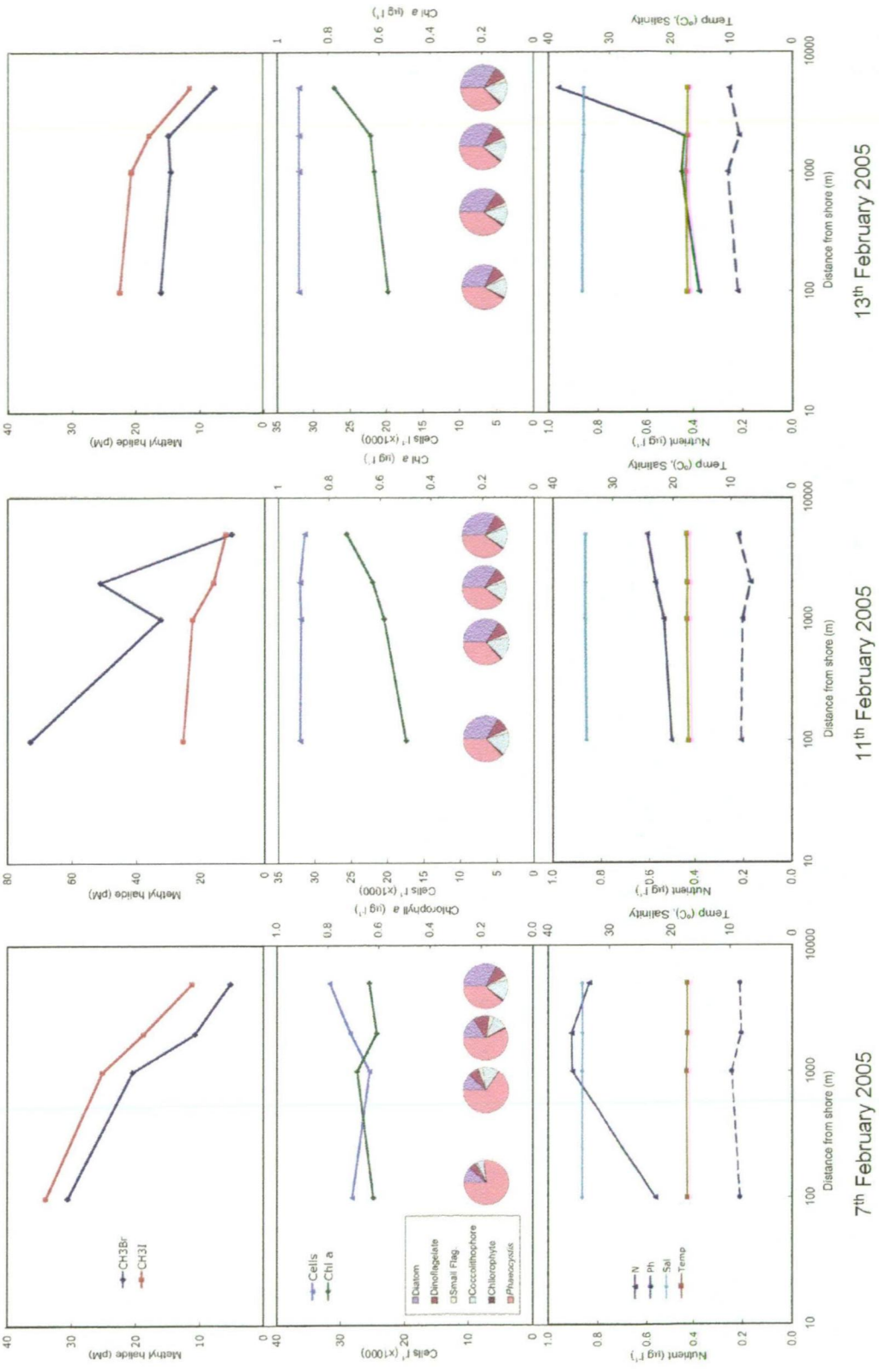

Figure 5.15 Methyl halide concentration, phytoplankton biomass and seawater properties on a transect off Cape Grim, February 2005

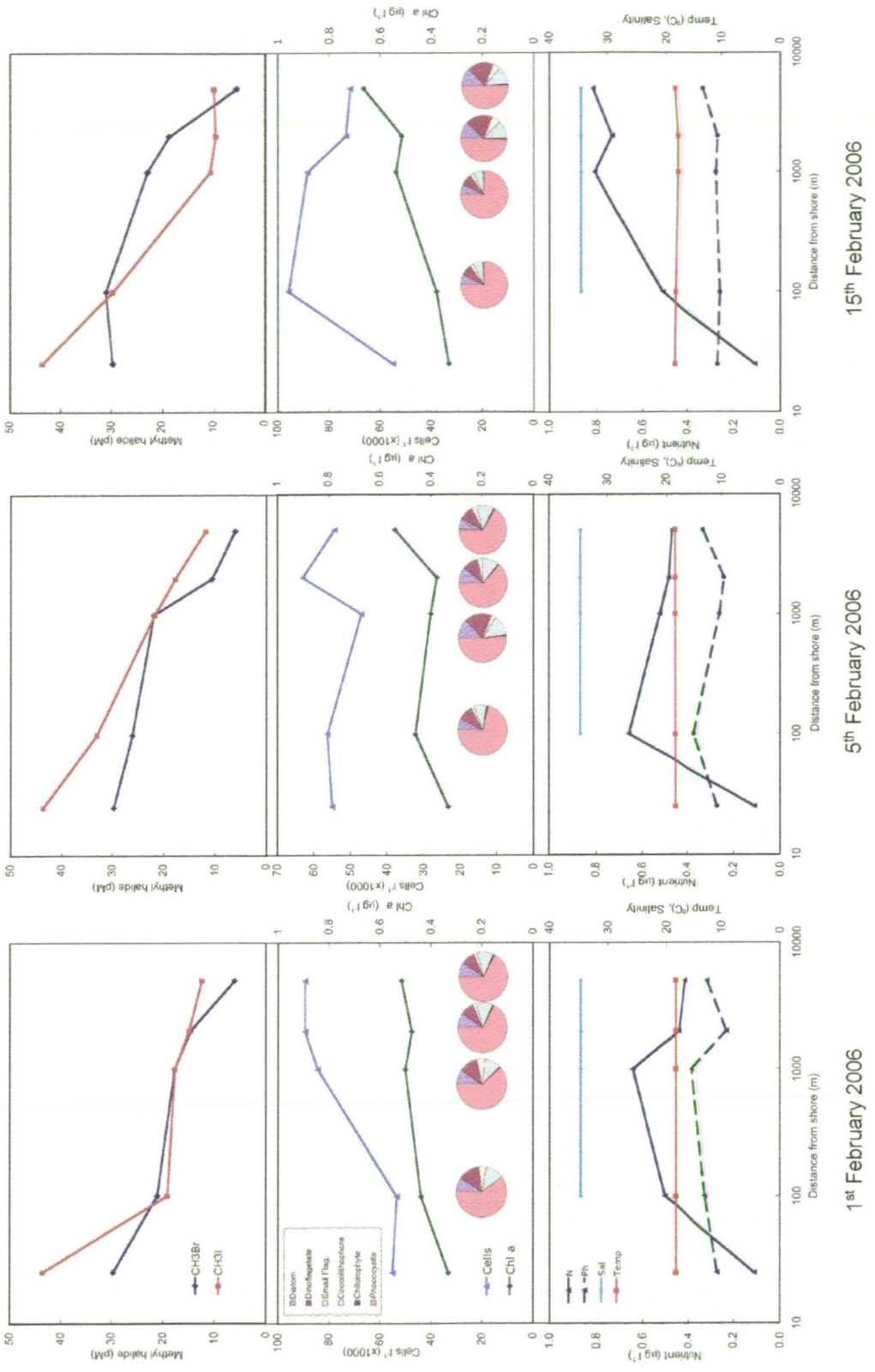

Figure 5.16 Methyl halide concentration, phytoplankton biomass and seawater properties on a transect off Cape Grim, February 2006

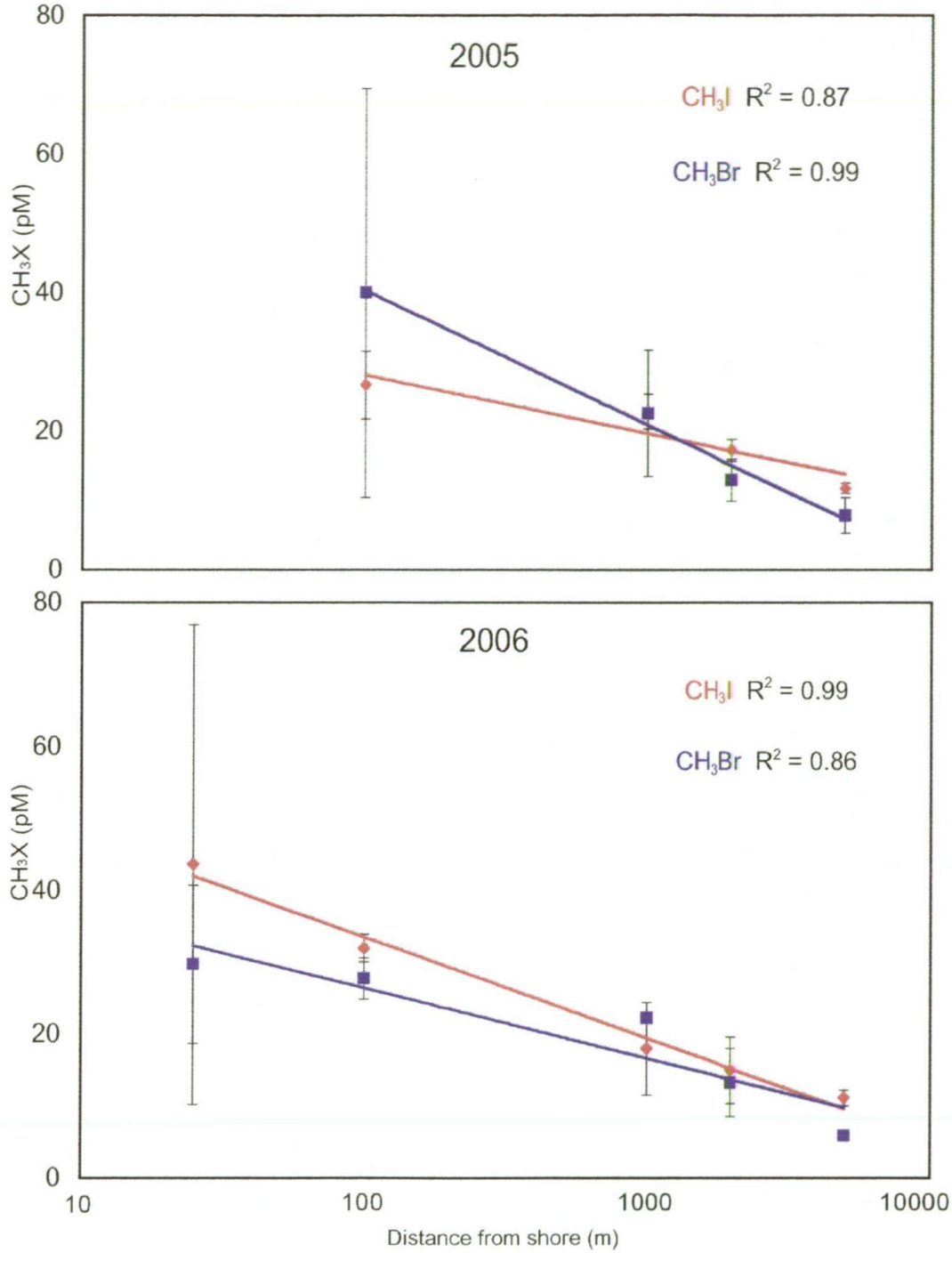

Figure 5.17 Average methyl halide seawater concentrations off Cape Grim in 2005 and 2006, fitted logarithmic trend lines and R^2 for log fit are shown, standard deviations shown, average of inshore measurements made in 2006 are included in plot and analysis

5.3.3 Kelp survey

Living bull kelp on the reef had an average density of 9 ± 4 plants m^{-2} and biomass of 82 ± 25 kg m^{-2}. This is within the range of measurements taken previously for this species of 0.8 to 23.5 plants m^{-2} and 4 to 108 kg m^{-2} (Cheshire & Hallam 1988a). It is at the lower range of density and the higher range of biomass found in this previous study, which is consistent with areas of high wave exposure (Cheshire & Hallam 1988a). Plants from higher wave exposure environments also have thicker laminae and are longer with more braids and have short, thick stipes (Cheshire & Hallam 1988b). This biomass is high compared to other seaweed communities. For comparison, *L. digitata* beds have an average biomass of 16 kg m^{-2} (Mann 1973), and typically around 2.5 to 5 kg m^{-2} at Mace Head (O'Dowd & Hoffman 2005). Kelp biomass and density were not measured at the less exposed Stanley site but kelp biomass was observed to be lower but in a similar order of magnitude to the Valley Bay site. .

Beach-cast kelp on the low-biomass region of the sandy beach at Valley Bay was present at an average of 2.5 kg m^{-2} representing a total mass of 7 tons. Beach-cast kelp was present on the area of high biomass region at the northern end of the beach at an average of 63 kg m^{-2} and a total mass of 82 tons. This makes a total of 89 tons on the beach. The period of sampling was observed to be a time of relatively high beach-cast kelp so the annual average would be expected to be somewhat lower than this.

5.4 Discussion

Methyl halide saturation was consistently positive, suggesting the inshore region is always a net source of methyl halides to the atmosphere. Methyl halide concentrations in seawater were elevated near the coast and decreased logarithmicly with distance from shore (Figure 5.17). There were also some higher concentrations of methyl halides in air directly above the kelp beds compared to air at the station (methyl bromide at Stanley, methyl iodide at Valley Bay). A large peak in methyl iodide was measured in seawater and air directly above kelp beds on the afternoon of

11th February 2006. A corresponding peak was not measured at the station. All these findings suggest that there are emissions of methyl halides from the coastal rocky reef and this effect is highly localized. It is likely that the source of this emission is macroalgae, mainly kelp. Identifying areas of high halomethane through measurements of seawater concentrations is limited since concentration reflects net accumulation and does not consider dilution, volatilization, exchange, photolysis and biodegradation (Manley *et al.* 1992). However, the high and persistent enrichments near *Macrocystis* kelp in California make it apparent that there is a major source (Manley *et al.* 1992). The same is true for these measurements.

The elevated concentrations of methyl halides within the kelp beds are expressed as enrichment factors in Table 5.1. Enrichments are found in the concentration of methyl halides in seawater within beds compared to outside of beds (measurements made at a site 5 km offshore in transects from the same year), and in the concentration in seawater within beds compared to open ocean seawater (average of open ocean measurements outlined in Chapter 3). Enrichment was also present in some measurements of the concentration in air above beds compared to summer baseline average concentrations outlined in Chapter 2. The greatest enrichment was found in methyl iodide on 11th Feb 2006.

The enrichment factor in seawater within seaweed beds and logarithmic decrease of methyl halide concentrations with distance from shore (Fig 5.17) were similar to that found near beds of *Macrocystis* kelp in California (Manley *et al.* 1992). A maximum enrichment of methyl iodide in seawater amongst kelp beds of 143 was lower then the value of 1000 found by Lovelock (1975). However, the enrichment factors are generally similar to those more recently found in seaweed beds in the UK and Ireland. Enrichment factors in seawater within kelp beds compared to 5 km offshore are similar to those found in rock pools (4.3 & 3.9 for methyl iodide, 1.4 for methyl bromide) and in beds of various kelp taxa (1.76 for methyl iodide) found by Baker *et al.* (2001) and Nightingale *et al.* (1995). Enrichment in air above kelp beds compared to a cliff top was similar to that found in England (1.5 to 2.5 for methyl iodide and 1.0 to 1.2 for methyl bromide) by Baker *et al.* (2001).

Table 5.1 Enrichment factors of methyl bromide and methyl iodide measured near coastal kelp beds of NW Tasmania

Year	Enrichment of	Compared to	Gas	Factor (av.)	Max
2005	Seawater near kelp	Water at 5 km	CH_3Br	3.3	8.2
			CH_3I	1.1	2.3
	Seawater near kelp	Open ocean	CH_3Br	13.1	32.6
			CH_3I	13.2	27.1
	Air over kelp	Air at station	CH_3Br	3.3	
			CH_3I	0.64	
2006	Seawater near kelp	Water at 5 km	CH_3Br	5.0	7.5
			CH_3I	2.5	5.1
			CH_3I 11th Feb		12.7
	Seawater near kelp	Open ocean	CH_3Br	15.2	22.6
			CH_3I	28.3	57.1
			CH_3I 11th Feb		143.1
	Air over kelp	Air at station	CH_3Br	0.4	
			CH_3I	1.7	
			CH_3I 11th Feb		3.7

Methyl halide concentration in seawater near kelp beds was variable over daily periods, far more so than at any station along the transects (Figure 5.7-5.12, 5.15-5.16). Carpenter *et al.* (1999) found a distinct negative relationship between tidal height and methyl halide seawater concentration, with peaks occurring at low tide. There were no consistent and predictable peaks of methyl halide concentration at low tide in these measurements. Some peaks were present at low or receding tide, including the large peak in methyl iodide on 11th Feb 2006, however the pattern of peaks was not consistent. The fit of a linear function to the relationship to light, tide and methyl halide concentration was poor for both methyl halides at both locations ($R^2 < 0.2$), and the fit of the flexible, non-linear additive model was also quite poor for both methyl halides at both locations ($R^2 < 0.4$). This simplified approach ignores correlations in the time series, but gives an indication that the relationships between tide, light and methyl halide concentration were not simple. Also, a pulse of methyl iodide was not observed following re-immersion after low tide, as it was for the laboratory study of *Ascophyllum* sp. (Nightingale *et al.* 1995). More frequent sampling would be required to fully assess the timing of peaks in methyl halide concentration, however from the data presented here it appears that there was no simple relationship between tidal height, light intensity and methyl halide peaks in

the inshore environment here and more variables are required to fully describe the variability of inshore methyl halide concentration.

The source of methyl halides from phytoplankton appeared insignificant compared to that from the reef, presumably kelp. There is no similarity between the spatial or temporal pattern of phytoplankton parameters (Chlorophyll *a*, cell number, photosynthetic yield) and methyl halide concentration in any daily profile or transect. Nitrate is depleted in the inshore waters compared to offshore, shown in the 2006 transects (Figure 5.16) and variable in the inshore waters of both Stanley and Valley Bay, shown in the daily profiles (Figure 5.7 to 5.13). This may infer some level of nutrient limitation to both phytoplankton and macroalgae near the shore.

5.5 Conclusions

The inshore waters at both Valley Bay and Stanley are a large and variable source of methyl halides. There is a logarithmic decrease in methyl halide concentration with distance from the high-biomass kelp beds at the shore out to 5 km, and the source from phytoplankton appears insignificant compared to that from kelp beds near the coast. There was only a partial influence of tidal height on the peaks in methyl halide concentration in seawater close to shore, and more variables are required to describe the variability. There was an isolated incident of very high emission of methyl iodide from the coast with an unknown trigger on 11th Feb 2006. This peak was not part of a regular or predictable pattern that is observable from the data presented here, and events such as this may happen only sporadically.

Chapter 6. Links between emission of methyl iodide, iodine and other gases from kelp beds and new particles detected at the Cape Grim station

6.1 Introduction

Iodine from biogenic sources in the ocean can undergo a series of chemical reactions to form particles of iodine oxide (O'Dowd *et al.* 2002b, see Chapter 1.9.3). Iodine containing gases and numerous other biogenic gases from the ocean and the coast may act as the precursor for the formation of new particles. This chapter examines the links between the emission of methyl iodide and other precursor gases at the coast at Cape Grim and the pathways of new particle formation in the coastal MBL during the "Precursors to Particles" summer 2006 campaign. Sections of the work reported in this chapter are published in the papers Grose *et al.* (2007), Cainey *et al.* (2007 a and b) included in Appendix 1.

The analysis of station data in Chapter 2 included the detection of 25 events of apparently coastal particle formation detected at the station over 3 years. One event on the 11th February 2006 fell within the campaign, and is of special interest here. Also, since iodine emitted from coastal kelp beds has been identified as a precursor to new particle formation at Mace Head (McFiggans *et al.* 2004, Saiz-Lopez *et al.* 2004), an investigation of the emission of iodine (I_2) from the dominant inter-tidal kelp (*Durvillaea potatorum*) is included.

6.2 Methods

6.2.1 Field measurements

Data was collected in the immediate vicinity of the Cape Grim station during the Precursors to Particles campaign from 1st to 18th February 2006. All data collected personally from this campaign is presented in Chapter 5. Methyl bromide is not implicated in particle formation, and so will not be discussed here.

The field data regarding methyl iodide presented in Chapter 5 is compared to data collected by others, including wind direction and speed, particles, DMS, methane, carbon monoxide, HFC-134a, iodine oxides (IO, OIO) and methyl iodide measured at the station. These measurements come from routine measurements taken during the campaign by CG-BAPS, AGAGE and also other measurements taken especially for the campaign. A general description of the campaign and the data collected is found in Cainey *et al.* (2007b). Particle monitoring is described in Chapter 2.2.3

6.2.2 Iodine emissions

An experiment was conducted in December 2006 to measure the direct emission of iodine (I_2) from bull kelp using a method adapted from Palmer *et al.* (2005). Fresh fronds of bull kelp (*Durvillaea potatorum*) were collected from the rocky reef in front of the Cape Grim BAPS and stored in fresh seawater until needed. Nine experiments were run, each using a separate frond of kelp weighing between 140 and 250 g. Each piece of kelp was towel-dried and placed in a sealed 1 litre conical flask and exposed to natural levels of solar radiation and ozone concentrations. Each run was performed under full sun on a sunny day between approximately 10am to 3pm.

Headspace air was sampled at 20, 40 and 60 minutes. At each time interval, air was pumped through a water trap of salt water and ice maintained at -15 °C to remove water vapour and then bubbled through analytical reagent grade ethanol to collect iodine gas as iodide, then through the pump and a gas flow meter. Ten litres of air was pumped through to ensure all dead-space was cleared. An ultraviolet spectrophotometer (Jasco UV1-DEC-100-V) was used to detect iodide collected in the ethanol, and calibrated with standards of potassium iodide (KI) made up to 5, 12.5, 25, 50 and 100 μM run twice daily. Blanks (with no kelp in the chamber) were also run daily. Experimental apparatus are shown in Figure 6.1 and 6.2.

Figure 6.1 Photograph of apparatus set up for measurement of iodine (I_2) emissions from bull kelp (*Durvillaea potatorum*), showing flask, cooling chamber, bubbler, pump and gas meter, Cape Grim station deck, December 2006

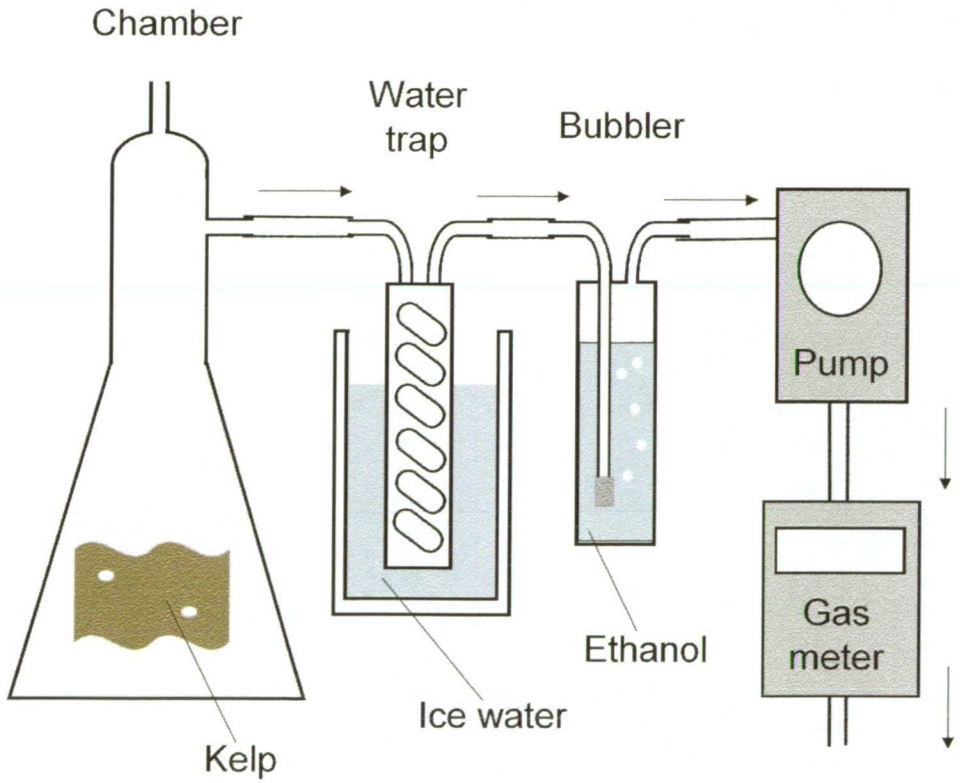

Figure 6.2 Schematic of apparatus for collection of I_2 gas from kelp in a chamber in A.R. grade ethanol bubbler trap, chamber opening was sealed during the experiments and opened for gas collection

6.3 Results

6.3.1 Field measurements

Wind, pressure, radiation and tide information is shown in Figure 6.3 and measured concentrations of particles and various gases are shown in Figure 6.4. During the campaign there were long periods of baseline conditions, periods of non-baseline are shaded in Figure 6.3. Four frontal systems were encountered, shown as dashed lines, three with no rain, one with rain. The largest frontal system was associated with a plume of smoke from a bushfire on nearby Robbins Island, reflected in the high particle, methane and carbon monoxide measurements.

DMS was measured by proton transfer reaction mass spectrometry (PTR-MS) only after the 17th February due to technical difficulties. DMS was generally < 0.15 ppb, except one peak following the bushfire plume. Iodine oxides (IO, OIO) were measured using multi axis differential optical absorption spectroscopy (MAX-DOAS) and a portable version of the same instrument, the mini-MAX-DOAS at the station and from the beach, and were consistently below detection levels (Cainey *et al.* 2007b). The alkyl halides CH_2I_2, CH_2IBr and $CHIBr_2$ were not measured during the campaign. These have previously been found to be under a detection limit of 0.04 pptv (Carpenter *et al.* 2003).

UFCN showed peaks during times of frontal passages and during periods of non-baseline conditions, with only minor peaks occurring during baseline conditions (Figure 6.4). These included a small peak (3720 cm^{-3}) on the afternoon of the 11th February and very minor peaks (<1000 cm^{-3}) on 4th and 5th February (Figure 6.4, 6.5). No events where small particles grew from the ultra fine condensation nuclei (3-10 nm) range to the CCN size (>30 nm) were observed during the campaign (Cainey *et al.* 2007b).

Methyl iodide measured at the station during the period of 1-17th February was 1.5 ± 0.3 pptv (Figure 6.5), with no distinct short-term peaks. Methyl iodide concentration in seawater near the kelp beds on each sampling day was 28.6 ± 13 pM (range 14.8 to 57.7 pM), except for the afternoon of 11th February 2006, when the concentration was above 63.3 pM, peaking at 144.5 pM at 4:00 pm (Figure 6.5 & 6.6).

Concentrations in air directly above the sea were measured to be 2.7 ± 0.6 pptv (range 2.1 to 3.8 pptv), except for 11th February 2006 where concentration was elevated, measured as 4.5 pptv in the morning and 5.5 pptv in the afternoon (Figure 6.5 & 6.6). Methyl iodide measured at the station did not show any distinct peaks at this time (Figure 6.6). The afternoon of the 11th February 2006 was at a time of receding tide and decreasing radiation (Figure 6.6). As noted in the last chapter, air mass origin on the 11th February 2006 was from the baseline sector of the Cape Grim wind profile, as shown by a back trajectory.

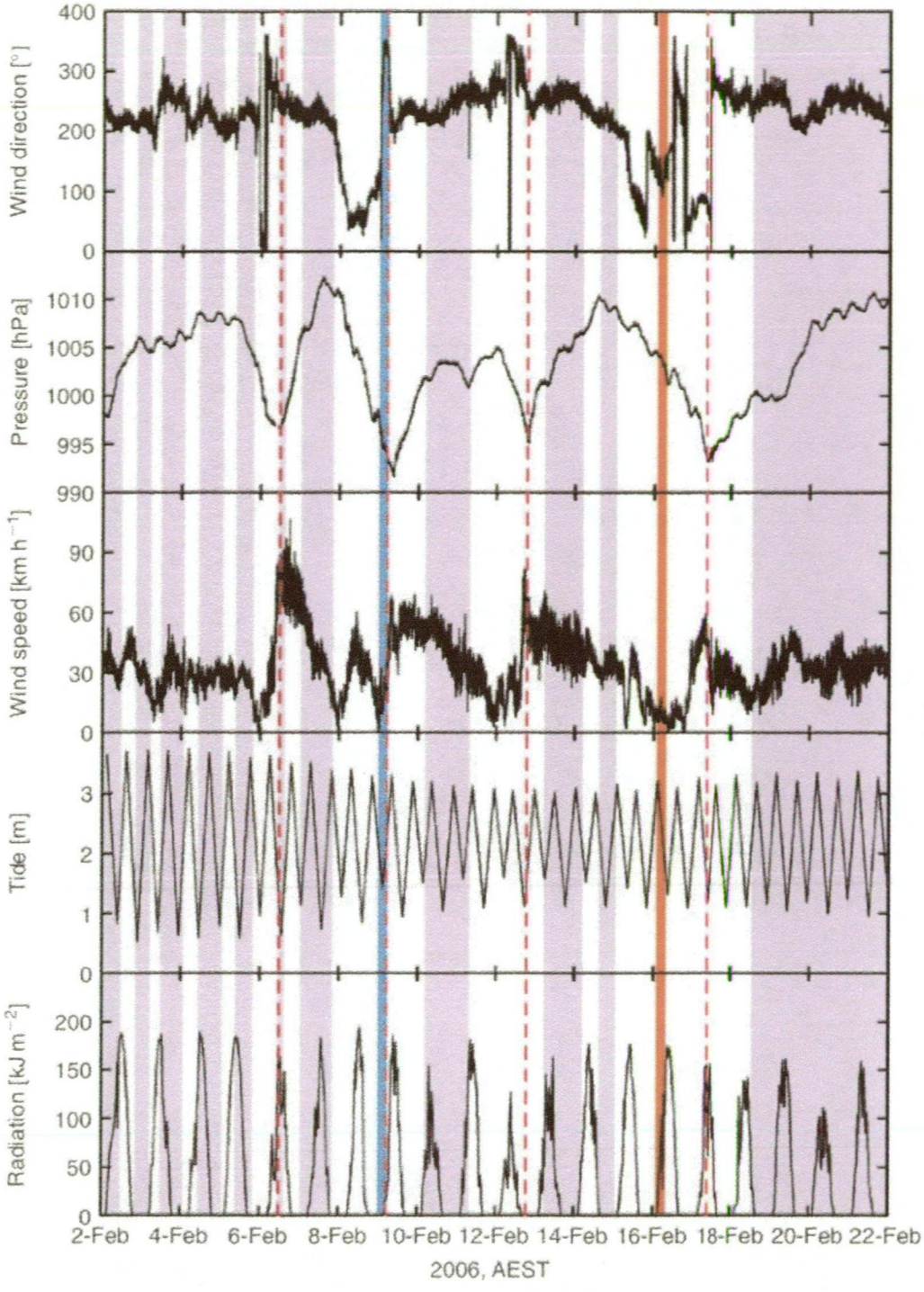

Figure 6.3 General conditions measured at Cape Grim during the Precursors to Particles (P2P) campaign, February 2006; red dashed lines represent the passage of fronts, blue shading represents significant rainfall (>0.2 mm), orange shading represents the period affected by a bushfire plume, purple shaded areas are non-baseline (Source: Cainey *et al.* 2007b)

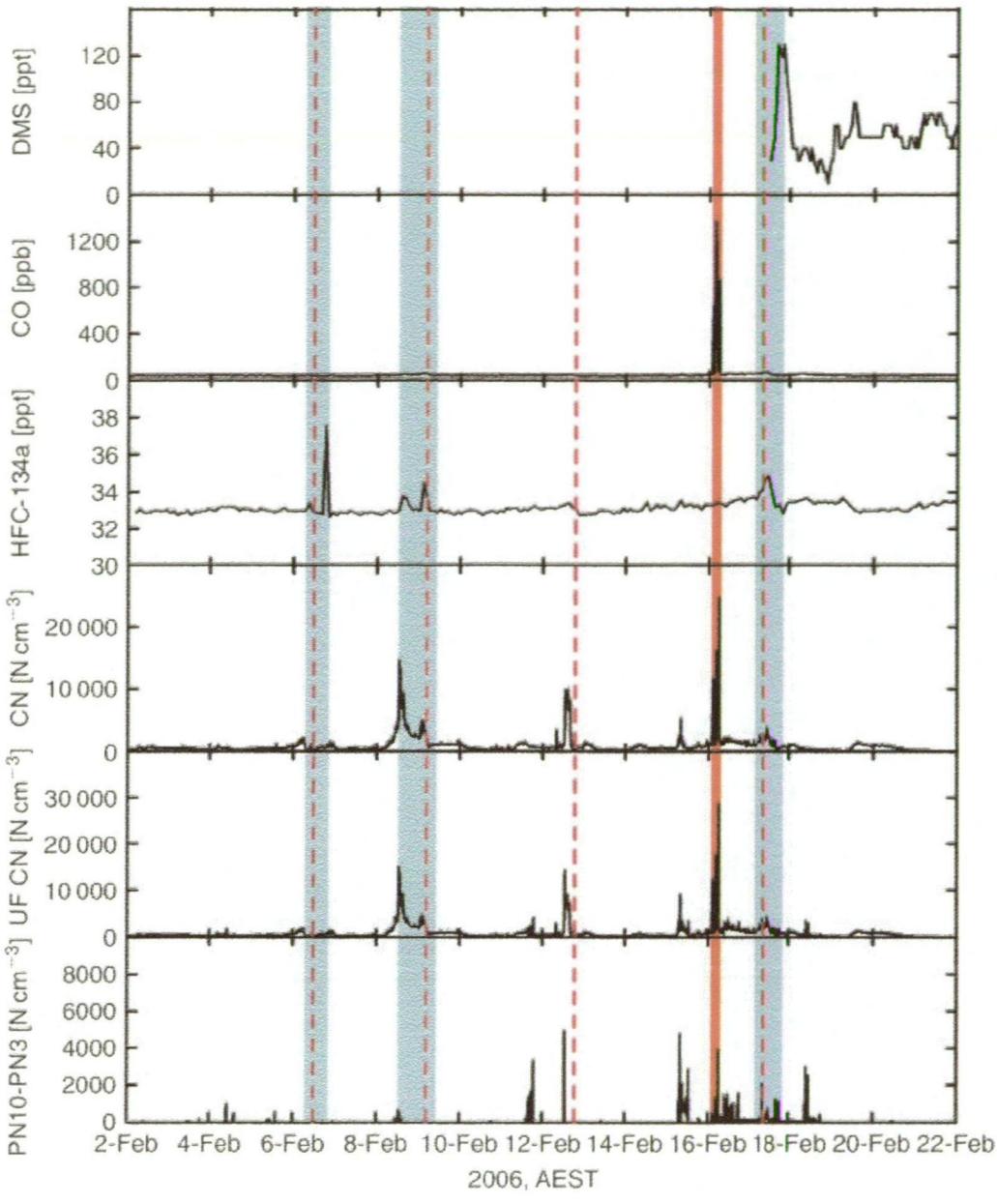

Figure 6.4 Precursor gases and particles at Cape Grim during P2P, February 2006; carbon monoxide is a marker for biomass burning (orange line represents bushfire plume); HFC-134a is a marker for air originating in Melbourne (green areas); red dashed lines represent the passage of fronts (source: Cainey *et al.* 2007b)

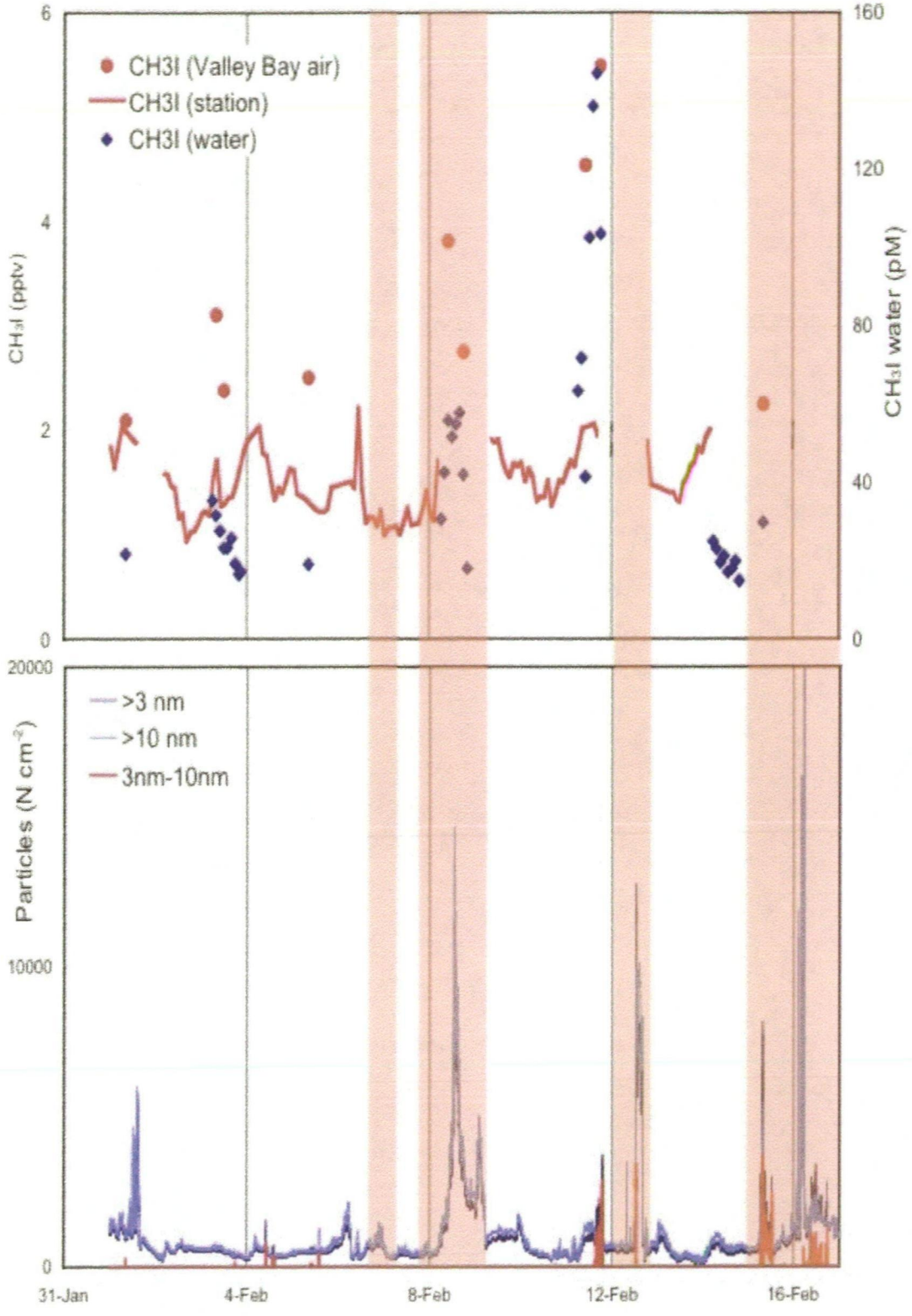

Figure 6.5 Methyl iodide concentration in Valley Bay air, in air at the station and in sea water near kelp beds, particle concentrations in various size ranges measured at the station measured during the P2P campaign 1-16 Feb 2006; yellow shading indicates approximate periods of non-baseline conditions longer than 4 hours

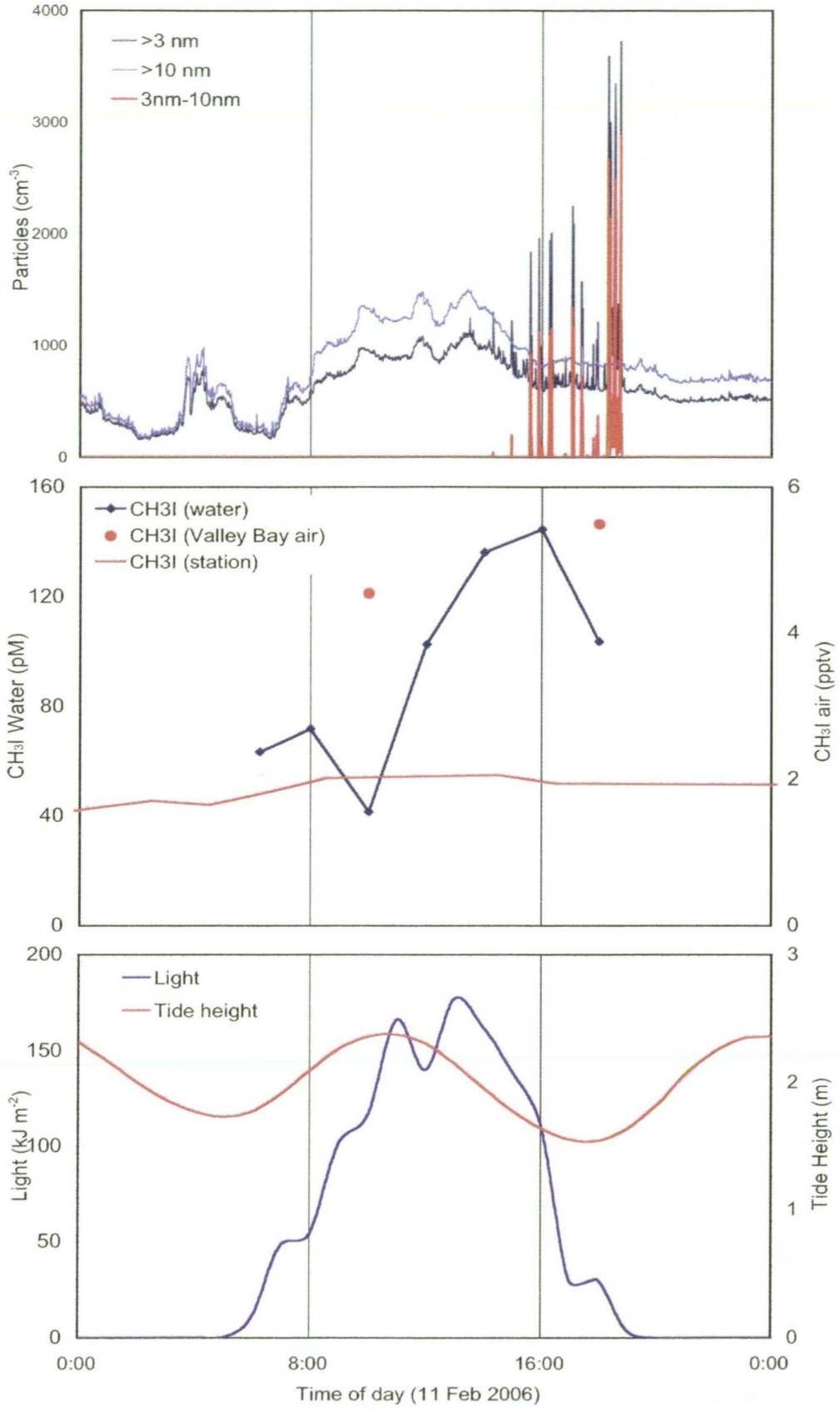

Figure 6.6 Particle concentration in baseline air at Cape Grim, methyl iodide concentration in Valley Bay air, station air and in Valley Bay seawater, tide height at Valley Bay and radiation measured at the station, 11th Feb 2006

6.3.1 Iodine emissions

One replicate was disregarded due to equipment failure, leaving eight successful replicates. Each replicate shows a similar pattern of emission, with relatively higher emission from 0 to 20 minutes (30.1 ± 11.3 pmol I_2 g^{-1} (FW) min^{-1}), followed by lower emission fluxes from 20 to 40 min and lower again from 40 to 60 minutes, shown in Figure 6.7. Averaged over the entire hour, the bull kelp emitted 18.1 pmol I_2 g^{-1} (FW) min^{-1}.

This is in the lower range of that found for *Laminaria digitata*, which emitted 0 to 9 pmol g^{-1} (FW) min^{-1} from unstressed kelp, and 24, 38 & 130 pmol g^{-1} (FW) min^{-1} from stressed kelp (Palmer *et al.* 2005).

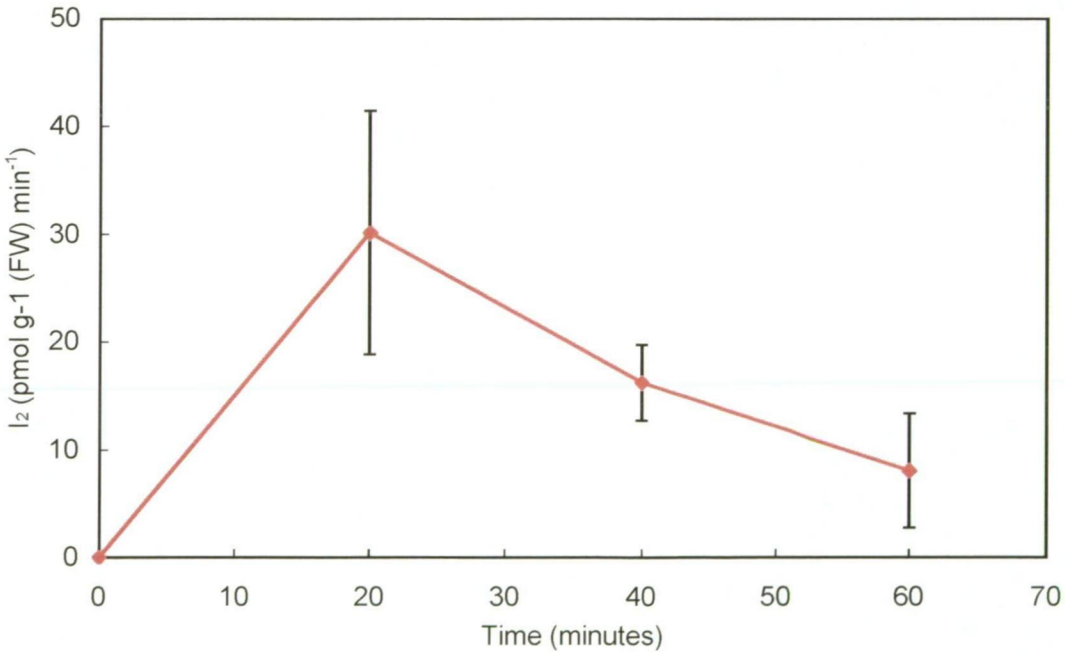

Figure 6.7 Emission of iodine (I_2) per fresh weight by bull kelp measured as a concentration of I_2 in a 2 litre chamber exposed to natural sunlight and ozone concentration

6.4 Discussion

6.4.1 Link between methyl iodide and particles

There is an apparent relationship between the period of elevated methyl iodide concentration in the coastal seawater and air above the sea surface on the afternoon of 11th February 2006 and a subsequent period of new particle formation. Air was considered baseline at this time, and a back trajectory showed the air was of marine origin. This provides indirect evidence that production of methyl iodide from an inshore marine origin is linked to a particle formation pathway during this event. This was the only event detected during the campaign and the analysis of station data in Chapter 2 showed that the detection of events of elevated numbers of new particles are rare. This suggests that the event on the 11th February 2006 was unusual rather than part of a regularly occurring process.

The atmospheric lifetime of methyl iodide at this latitude in summer has been estimated as 4 to 5 days (Cohan *et al.* 2003). Therefore, the methyl iodide emitted from the inshore environment did not directly act as a precursor to new particle formation in this instance, as the methyl iodide emitted at the coast would not be broken down into iodine until far from the station vicinity. However, the data do suggest that the elevated concentration of methyl iodide was coincident with, and possibly linked to, a peak in concentration of another unknown precursor gas. The source of this other precursor gas may have been emissions from the kelp on the reef or from the beach-cast kelp on the shore.

6.4.2 Iodine precursors

Bull kelp emitted modest levels of iodine (I_2) under natural stress, 18.1 pmol I_2 g^{-1} (FW) min^{-1}, which is up to 7 times less than *Laminaria digitata* (Palmer *et al.* 2005). The lower emission may be at least partly related to the iodine content of the kelp. The iodine content of *D. potatorum* has not been reliably measured, but some preliminary work has reported a content of approximately 90 mg kg^{-1} (Ma, *pers. comm.*[1]). This is much lower than many other kelp species including *L. digitata*,

[1] Ma, G. Westmead Hospital, Sydney NSW, Iodine content of *Durvillaea potatorum*, unpublished data

which contains 7500 to 12000 mg kg^{-1} in winter, 2500 to 6000 mg kg^{-1} in summer and up to 50,000 mg kg^{-1} in young plants (Ar Gall *et al.* 2004).

It is thought that direct emission of I_2 from macroalgae provides a major precursor for the formation of particles of iodine oxide at Mace Head (McFiggans *et al.* 2004; Saiz-Lopez *et al.* 2004, Saiz Lopez & Plane 2004; O'Dowd & Hoffman 2005). The formation of particles of iodine oxide and the significance of I_2 as a precursor are unknown at Cape Grim. Unfortunately, I_2 emitted directly from kelp was not measured in the field during the campaign, and so its significance in the specific event on 11th February is unknown. It is possible that elevated emission of methyl iodide was associated with a period of high I_2 emission and this provided a precursor to particle formation. However, the low iodine emission from bull kelp measured in the laboratory indicates that the kelp are unlikely to provide the minimum threshold concentration of 10 pptv of I_2 in air required for this particle formation, shown from a chamber study (Saiz-Lopez & Plane 2004).

The alkyl halide CH_2I_2 has previously been suggested as an important precursor to the formation of particles of iodine oxide (Carpenter *et al.* 1999). Measurements of the alkyl halides including CH_2I_2 have been previously measured to be below a detection limit of ~0.04 pptv at Cape Grim, unlike at Mace Head (Carpenter *et al.* 2003). Emission of CH_2I_2 from kelp may result in an enriched concentration immediately above the kelp beds not detected at the station, however it appears unlikely that the minimum threshold concentration of 15 pptv for particle formation shown from chamber studies (Jimenez *et al.* 2003) would be present from this source.

Also, the absence of detected iodine oxides in the boundary layer by DOAS throughout the campaign suggests that the formation of particles from any iodine precursor was unlikely.

6.4.3 Other precursors

The concentrations of another gas that can act as a precursor to particle formation, DMS, was not monitored until the 17th February, so its concentration during this event is unknown.

The first report from the Cape Grim station noted that on infrequent occasions in winter and spring when it was both calm and sunny, particle concentrations would sometimes exceed 20,000 cm^{-3}, and these events were accompanied by the smell of rotting kelp (Baseline 1978). Bigg & Turvey (1978) showed that the source of the particles was piles of kelp on the beach below the station, and confirmed the effect only occurred during sunny days of winter and spring. Investigation of the formation of new particles above stressed kelp in a flux chamber was carried out as part of the campaign (Cainey *et al.* 2007a, Appendix C). Particles were detected above stressed kelp when exposed to excess ozone, and transmission electron microscopy indicated the particles had a structure consistent with aromatic volatile organic compounds. These particles were only observed to form above kelp when the ozone level was elevated above the natural range. However, there may be some emission of organic compounds from kelp at natural levels of ozone that was not detected in this limited experiment.

This suggests that the period of elevated methyl iodide concentration on the 11th February 2006 may be concurrent with direct emission of aromatic volatile organic compounds from the kelp, and these compounds coalesced into particles that were detected at the station. Further evidence would be required to confirm this assertion. Various volatile organic compounds (Galbally *et al.* 2007, Fletcher *et al.* 2007) as well as viruses' (Bigg 2007) were also implicated in the particle formation and growth processes during the 2006 campaign.

6.4.4 Significance of coastal particle bursts

The maximum particle number during this event was small compared to coastal particle bursts from iodine precursors at Mace Head. The count of particles in the 3-10 nm range in a 1 minute scan peaked at 2874 cm^{-3}. The maximum count of UFCN was 3720 cm^{-3}, compared to a typical burst of UFCN during an event at Mace Head of 598,900 cm^{-3} on 5th April 2004 (Yoon *et al.* 2006), a difference of two orders of magnitude. A comparison of these events is shown in Figure 6.8.

This event also appeared to have a different timing compared to the Mace Head events. The peak in particle number at Cape Grim at or near low tide occurred

towards the end of the day rather than near midday (e.g. Figure 6.8). This may be partially due to the westerly aspect of the beach and the presence of the cliff meaning the kelp is exposed to more light later in the day. Or it may indicate a different particle formation process from that at Mace Head.

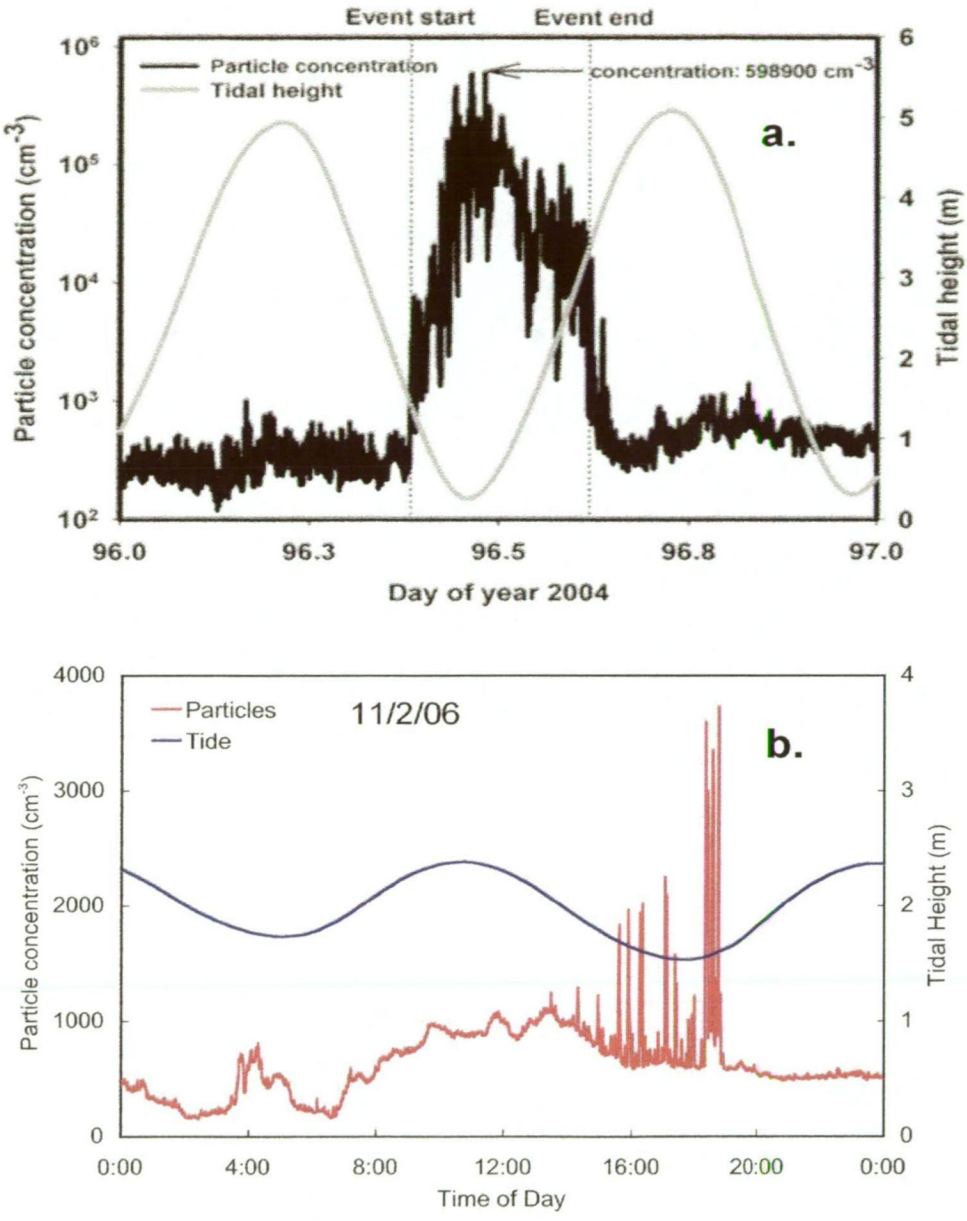

Figure 6.8 UFCN concentration measured during low tide coastal particle nucleation events at a. Mace Head (Yoon *et al.* 2006), and b. at Cape Grim

The maximum hourly average count of particles 3-10 nm in this event was 247 cm^{-3}. This was one of only 25 occasions where hourly average particle counts 3-10 nm were elevated >200 cm^{-3} above the monthly mean in baseline air at the station in 2004-2006, and all events showed hourly average particle counts in the 3-10 nm

range of less than 600 cm^{-3} (Chapter 2). This was one of only seven events occurring during a sunny day and coincident with low tide. Also, particle growth from the 3-10 nm size range to the >30 nm size and further into CCN-sized particles was not observed associated with this event (Cainey *et al.* 2007b). There was no regular and predictable detection of new particles associated with low tide, either during the campaign or detected in station data presented in Chapter 2, as was found at Mace Head. This suggests that these coastal particle events are both infrequent and minor in importance.

The trigger for the period of elevated methyl iodide on this day and not others is not clear. Methyl iodide peaked during receding tide and afternoon sun, inferring some degree of photo-oxidative stress to the kelp. However, the peak in methyl iodide began in the middle of the day when tide was high, and the detection of new particles that followed the peak in methyl iodide occurred between 4:00 to 7:00 pm, when light was fading. In addition, there was no regular and predictable pattern of methyl iodide emissions associated with low tide on each day, with only one incident of elevated methyl iodide found during the campaign. Low nitrogen concentration and N:P ratio (see Chapter 5) suggests kelp may experience some nutrient stress. However, the conditions during this period were not exceptional, and similar levels of stress would be present on other days.

6.5 Conclusions

There are periodic pulses in the source of methyl iodide at the coast, leading to episodes of elevated flux to the atmosphere. This elevated flux was concurrent with detection of new small particles on one sampling day. Methyl iodide did not act as a precursor to new particles, but the peak in methyl iodide emission is likely to have been simultaneous with a high flux of other unmeasured gases that acted as precursors to new particle formation, such as aromatic compounds measured in a flux chamber experiment. The cause of this event is not clear, however photo-oxidative and nutrient stresses were likely to be present.

Several factors suggest that the emission of I_2 or iodinated gases by kelp in this region are less important contributors to bursts of new particles that then can grow

into viable CCN for cloud formation compared to Mace Head. There were no regular and predictable bursts of new particles at every low tide and full sun as is found at Mace Head during summer (Yoon *et al.* 2006). In addition, the one measurement of new particle concentration during baseline conditions was low compared to other locations, and failed to undergo growth into CCN. It appears that following particle nucleation, the subsequent mechanisms of particle growth were not present or not strong enough to create CCN. However, it appears that a minor particle formation pathway present in the inshore environment is associated with a high methyl iodide emission.

Chapter 7. Summary and conclusions

The data provided here depicts a dynamic and variable source of methyl halides from photochemical and biological production in the ocean, with no simple controlling variables or easily predictable patterns.

Monitoring of baseline air at the Cape Grim Baseline Air Pollution Station in 2004 to 2006 showed the concentration of methyl bromide had a small variability with no simple seasonal cycle (7.3 ± 0.15 pptv), and methyl iodide showed a distinct seasonal cycle (1.62 pptv autumn maximum, 0.87 pptv spring minimum). The small and complex temporal pattern of methyl bromide concentration was consistent with the previous hypothesis of a complex interaction of out-of-phase sources and sinks (Simmonds *et al.* 2004) and a longer lifetime. The larger and more simple seasonal cycle of methyl iodide was well correlated to SST in the adjacent ocean and was consistent with sources from both photochemical and biological production of methyl iodide in the surface ocean, each with temperature dependence and a time delay. There were numerous short-term peaks above the general trend that were related to stronger local sources. Methyl iodide showed a daily cycle with an afternoon minimum, demonstrating that methyl iodide more readily undergoes photolysis than methyl bromide.

The concentration and temporal variability of methyl halides in baseline air measured at the station can be almost entirely related to the ocean sources and sinks of these gases in the adjacent Southern Ocean, with some influence on the methyl bromide concentration from long-distance transport. A diagram showing the marine sources and sinks is found in Figure 7.1. Seawater concentration of methyl halides was highest at the coast, decreasing in a logarithmic relationship out to 5 km and continuing to decrease out across the continental shelf (Figure 7.2). Correspondingly, saturations were strongly positive in the coastal waters and fell to near equilibrium in the open ocean. The results collected here suggest that the inshore and coastal waters are consistently a source of methyl halides with periods of higher production. These waters may also represent a source of short-term increases in methyl halide concentration measured at the station. The open ocean in this region was a minor source or sink of methyl halides during the sampling period in late summer. It is

expected that the wider ocean provides the major source represented in the measurements at the station.

The pattern of decrease in methyl halide concentration with distance from the shore is similar to measurements made in the temperate waters of the northern hemisphere. This is seen in measurements of methyl iodide at Cape Grim and those at Mace Head, Ireland (Carpenter *et al.* 1999 and Baker *et al.* 2000), shown in Figure 7.3.

Methyl iodide concentration in the open ocean appears broadly correlated with inorganic iodide concentration, with some small differences. This relationship is consistent with linked or possibly synergistic production of both these species, possibly from biological inter-conversion by phytoplankton and bacteria.

There was no strong seasonal cycle in methyl halide concentration in coastal seawater. This is in contrast to the temperate waters of the English Channel (Archer *et al.* 2007). There is a complex set of controlling factors contributing to the marine methyl halide source in this region, with evidence for some production from phytoplankton, especially during high-biomass events. An increase in methyl halide concentration was seen during a bloom of diatoms of the genus *Chaetoceros*.

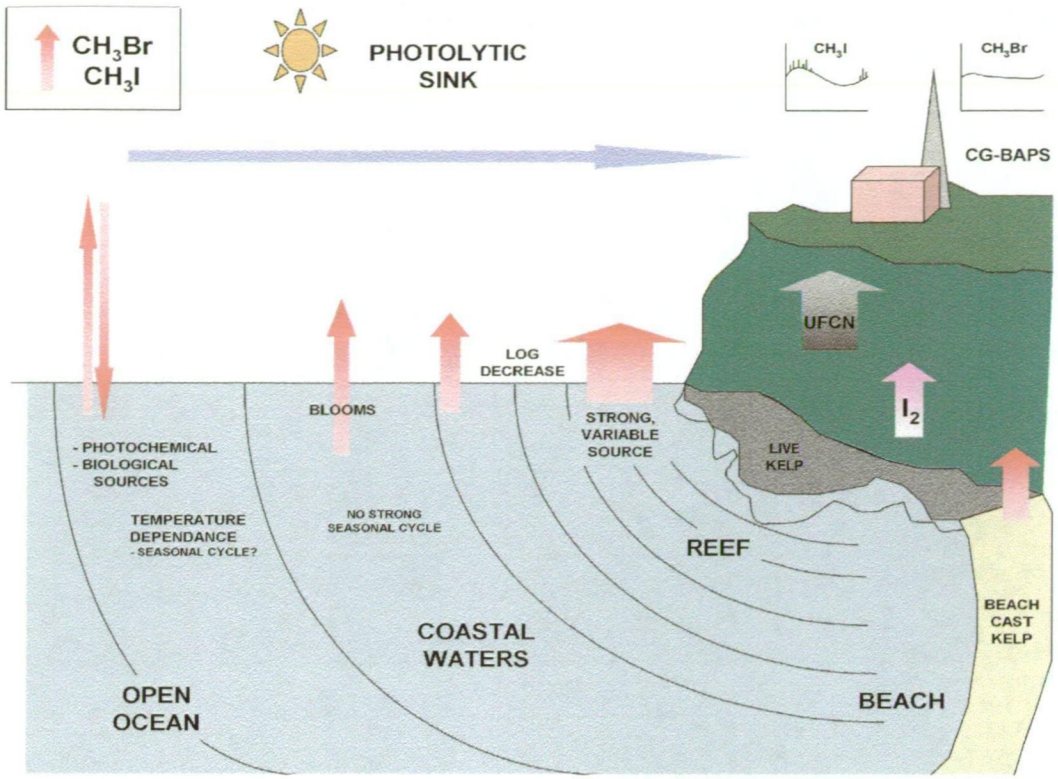

Figure 7.1 The Cape Grim region, showing location and characteristics of the marine sources of methyl halides to the atmosphere that are measured at the station, and fluxes of I_2 and UFCN

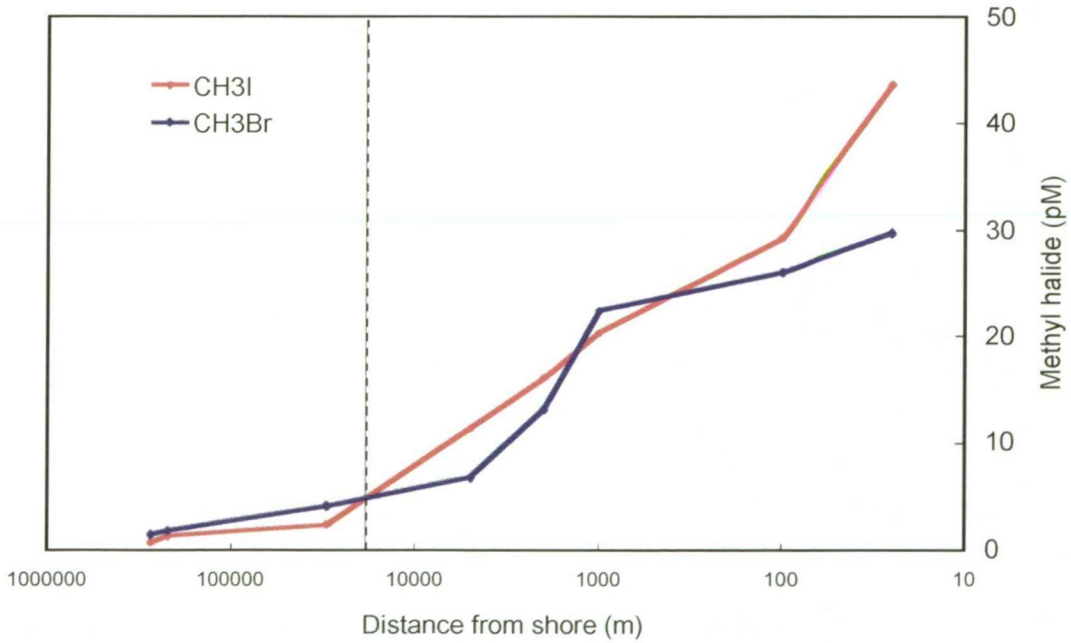

Figure 7.2 Average seawater concentrations of methyl bromide and methyl iodide in the waters off Tasmania with distance from shore

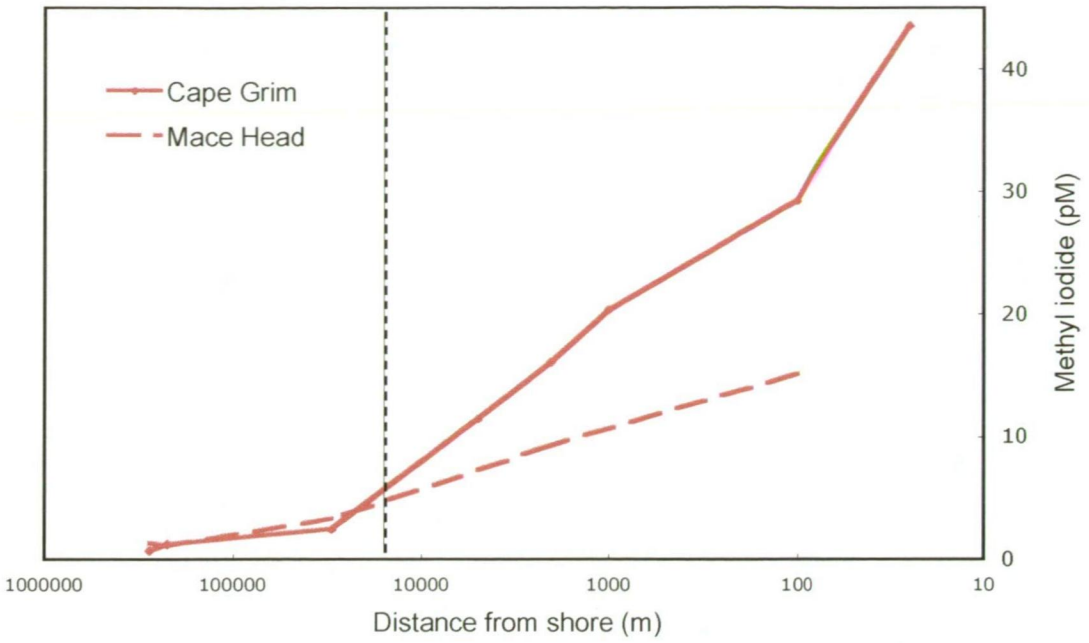

Figure 7.3 Measurements of methyl iodide concentration in seawater with distance from shore at Mace Head (Carpenter *et al.* 1999, Baker *et al.* 2000) averages of measurements from this work (Cape Grim)

There is a localised source of methyl halides from beds of bull kelp (*Durvillaea potatorum*) on the rocky reef adjacent to the station and beach-cast kelp on the beach south of the station. This is indicated through numerous enrichments of methyl halides among the kelp compared to further away (see Chapter 5). This source is highly localized and doesn't seem to be detectable at the station. The concentration of methyl halides among the kelp was highly variable, with a statistically insignificant correlation to photo-oxidative stress on kelp (light and tide), and must therefore be dependant on other unknown controlling variables as well.

An event of particularly elevated methyl iodide measured in the inshore environment (11th February 2006) was followed by the detection of new particles at the station. This unusual event occurred in the afternoon of a sunny day during a receding tide, indicating it may be related to photo-oxidative stress on the kelp. The cause of the event on this particular day and not others is unknown since the conditions were similar to those on other days. The subsequent peak in particle number at the station could not be due to methyl iodide acting as a precursor since the lifetime of methyl iodide is a few days. However, the peak in methyl iodide may have been concurrent

with the emission of other precursor gases from the kelp or emission of particles directly from the kelp.

The kelp emitted moderate amounts of iodine gas (I_2) in laboratory experiments (18.1 pmol I_2 g^{-1} (FW) min^{-1}), however the contribution of iodine to particle formation (after Saiz-Lopez *et al.* 2004, McFiggans *et al.* 2004) in this instance is unknown. Formation of particles of aromatic organic compounds associated with bull kelp has been demonstrated (Cainey *et al.* 2007a) and may be the source of particles during this event. Whatever the specific mechanism, there appears to be some form of biogenic emission from kelp leading to particle formation. This emission was coincident with elevated methyl iodide emission in this incident.

This event and 25 other similar incidents were detected at the Cape Grim station in Jan 2004 – Dec 2006. After applying a strict baseline filter, 26 events of an hourly average particle count 200 cm^{-3} or more above the monthly mean were detected. These events occurred between October and March with some events occurring in the early morning and some in the late afternoon. Not all events were at or near low tide. This suggests that these types of coastal particle formation events are rare, and there are not regular and predictable events associated with low tide as was found at other location such as Mace Head (Yoon *et al.* 2006). Hourly average particle number in general also showed a similar pattern as these high events, with a peak in October, a smaller peak in January and a daily cycle consisting of peaks in the early morning and late afternoon.

The particle counts of these events were modest compared to events at Mace Head. For the February 2006 event, the maximum count of particles sized 3-10 nm was 2874 cm^{-3} and the maximum hourly average was 246 cm^{-3}. The corresponding maximum count of UFCN was 3720 cm^{-3}, which is low compared to a typical burst of UFCN from a coastal source at Mace Head which can reach up to 598,900 cm^{-3} (Yoon *et al.* 2006). Also, particle growth from the 3-10 nm size range to the > 30 nm size and further into CCN-sized particles was not observed during with the February 2006 event.

There are some similarities in the methyl halide cycle between Cape Grim region and other areas of similar latitude and climate, and some important local differences. This highlights the need for spatial coverage when accounting the global budgets of trace gases such as methyl halides. To fully understand the sources, sinks and fluxes of these gases, the influence of local physical conditions as well as the biological systems and their interactions must be considered. The results presented in this thesis shed some light on a small section of the complex, multifaceted ocean-atmosphere system. It also highlights the need for wide-ranging monitoring as well as multi-disciplinary study to understand the complex interactions and cycles of the earth system.

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Appendix. Published work

Appendix 1. Grose et al. *2007*

RESEARCH FRONT

Research Paper

CSIRO PUBLISHING

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Coastal marine methyl iodide source and links to new particle formation at Cape Grim during February 2006

Michael R. Grose,[A,C] *Jill M. Cainey,*[B] *Andrew McMinn*[A,C] *and John A. E. Gibson*[A]

[A]Institute of Antarctic & Southern Ocean Studies, Private Bag 77, Hobart, Tas. 7000, Australia.
[B]Cape Grim Baseline Air Pollution Station, 159 Nelson Street, Smithton, Tas. 7330, Australia.
[C]Corresponding author. Email: mgrose@utas.edu.au

Environmental context. Emissions of methyl iodide of a biological origin from inshore and coastal waters can be an important component of the atmospheric budget of iodine. Iodine from this and other sources is important in the natural ozone cycle in the troposphere and stratosphere, and may play a role in the formation of new small particles that can then grow to seed clouds. The specific coastal ecology at each location is important to the magnitude and characteristics of this methyl iodide source.

Abstract. Methyl iodide concentration in seawater and in the air directly above the sea was measured at an inshore site adjacent to the Cape Grim Baseline Air Pollution Station (Cape Grim BAPS) near a bed of Bull Kelp (*Durvillaea potatorum*) over daylight cycles and along a transect out to 5 km offshore. Most inshore samples had low and variable methyl iodide concentrations in seawater (14.8–57.7 pM) and in air immediately above the sea (2.1–3.8 parts per trillion by volume), with a partial tidal influence. A period of elevated methyl iodide concentration in the water (144.5 pM) and in air above the sea surface (5.5 pptv) was immediately followed by a measurement of new particles at the Cape Grim BAPS. This correlation provided indirect evidence that emission of methyl iodide from kelp is connected to the new particle formation pathway, but there was no evidence of a direct causal link. Elevated levels of atmospheric methyl iodide were not detected at the station (adjacent to the site but on top of a 94-m cliff) at the same time, which suggests the effect was localised above the sea surface. A rapid decrease of methyl iodide out to 5 km suggested that a source at the coastal reef was greater than from pelagic phytoplankton; this source could be the intertidal kelp beds.

Additional keywords: aerosols, biogenic production, halogen compounds, kelp, marine chemistry, methyl iodide.

Introduction

The biological production and release of methyl iodide provides a transport vector for iodine from the ocean to the atmosphere. Once released from the sea, iodine plays a role in the natural ozone cycle in the troposphere, and is also important in the transport of iodine onto land where it is an essential micronutrient for many organisms. Iodine is thought to play an important role in the formation of ultrafine new particles in air that can then grow to form cloud condensation nuclei (CCN)-sized particles and seed cloud formation. In the ocean, the major biological group that produces methyl iodide is the algae, both phytoplankton and macroalgae.

Organic iodine gases emitted from the sea to the atmosphere undergo photolysis to form inorganic iodine. Through a complex pathway of gas phase chemistry, iodine is thought to form solid particles of iodine oxide (aerosol) by a mechanism proposed by O'Dowd et al.[1] The composition of the particles is thought to be I_2O_4 [1] or I_2O_5,[2] iodine-containing gases that can act as precursors in this particle formation process have been measured at high levels in the marine boundary layer at coastal sites.[3–5] However, the majority of measurements of particle formation from iodine are from the restricted geographic area of the Mace Head research station in Ireland. Immediately south of the Mace Head station there are extensive beds of Oarweed (*Laminaria digitata*), which has an exceptionally high iodine content. Measurements at other locations with different conditions are sparse, therefore, the global significance of new particles from an iodine origin remains largely unquantified.[1,9] In addition, the dominant form of the iodine precursor, i.e. either organic iodine-containing gas or from elemental iodine (I_2), remains unclear for other locations.

Studies at Mace Head initially indicated that the emission of alkyl halides (e.g. CH_2I_2, CH_2ClI, CH_3I) from kelp and the surrounding ocean, which are then photolysed to produce I atoms and then IO by reaction with O_3, was a dominant pathway to new particle formation.[3,6] Laboratory experiments demonstrated that this process occurred under a range of conditions down to near atmospheric levels of CH_2I_2, ozone and radiation.[7–9] Recent work has revealed that a substantial iodine source is I_2 emitted directly from macroalgae at low tide, and this may be the dominant pathway to new particle formation.[10,11]

In the open ocean, organic iodine as methyl iodide is produced and emitted by phytoplankton.[12–14] Flux rates of methyl iodide from phytoplankton are generally small, e.g. 15 nmol m^{-2} day^{-1} in the Southern Ocean,[13] but the overall global flux is significant because of the large geographic area. However, at a temperate inshore site, the flux of iodine from phytoplankton is likely to be far lower in magnitude than that from macroalgal beds.

Here we present data on the source of methyl iodide produced biologically by phytoplankton and macroalgae in the coastal waters off Cape Grim, Tasmania, during February 2006 (the Precursors to Particles campaign). We investigated whether the

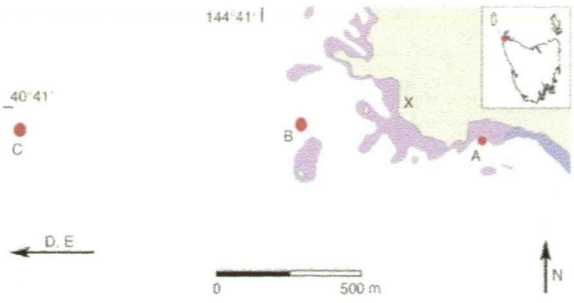

Fig. 1. Cape Grim BAPS area in north-west Tasmania, showing the approximate size and position of rocky reef and sandy beach. (X) Station building (40.683° S, 144.689° E), (A) inshore sampling site, (B) 100-m sampling site, (C) 1-km sampling site. The 2-km and 5-km sites (D, E) are not shown.

major source was from macroalgae or phytoplankton, and if there were any links to particle formation processes. Measurements of the physical conditions in the ocean are also presented to give context to the potential biogenic source of methyl iodide.

Results

Site and kelp bed description

The work was undertaken in the immediate vicinity of the Cape Grim Baseline Air Pollution Station (Cape Grim BAPS, Fig. 1). An exposed rocky reef with high wave action is adjacent to the station, at the base of a 94-m cliff. Next to the reef is a sandy beach. The dominant intertidal macroalgal species on the reef is Bull Kelp (*Durvillaea potatorum*). Bull Kelp was measured to have an average density of 9 ± 4 plants m^{-2} and a biomass of 82 ± 25 kg m^{-2}, which is within the range of measurements taken previously for this species of 0.8–23.5 plants m^{-2} and 4–108 kg m^{-2}.[15] This biomass is high compared with other seaweed communities. For comparison, *L. digitata* beds have been measured at 16 kg m^{-2}, and typically around 2.5–5 kg m^{-2} around at Mace Head.[16] Beach-cast kelp of various species was present on the sandy beach at an average of 63 kg m^{-2} (high biomass area, north end nearest the station) and 2.5 kg m^{-2} (low biomass area).

The iodine content of *D. potatorum* has not been reliably measured, but some preliminary work has reported a content of ~90 mg kg^{-1}.[17] This is much lower than many other kelp species including *L. digitata*, which contains 7500–12 000 mg kg^{-1} in winter, 2500–6000 mg kg^{-1} in summer, and up to 50 000 mg kg^{-1} in young plants.[18] A laboratory measurement showed that I_2 is emitted from *Durvillaea potatorum* kelp under natural levels of photo-oxidative stress at a rate of 18.1 pmol g^{-1} (FW) min^{-1}.[19] This is in the lower range of that found for *Laminaria digitata*, which was 0–9 pmol g^{-1} (FW) min^{-1} from unstressed kelp, and 24, 38, and 130 pmol g^{-1} (FW) min^{-1} from stressed kelp.[20] In addition, direct emission of new particles that contain aromatic compounds from *D. potatorum* has been demonstrated.[19]

Measurements

Methyl iodide concentration in seawater near the kelp beds on each sampling day was 28.6 ± 13 pM (range 14.8–57.7 pM) (Fig. 2), except for the afternoon of 11 February 2006, when the concentration was consistently above 63.3 pM, and peaked at 144.5 pM at 1600 hours (Figs 2 and 3). Concentrations in air directly above the sea were measured to be 2.7 ± 0.6 parts per trillion by volume (pptv) (range 2.1–3.8 pptv), except for 11 February 2006 when the concentration was elevated and measured as 4.5 pptv in the morning and 5.5 pptv in the afternoon (Figs 2 and 3). Methyl iodide measured at the station was measured as 1.5 ± 0.3 pptv, and did not show a distinct peak outside of the normal range on the afternoon of 11 February 2006 (Figs 2 and 3). Air mass origin on the 11 February 2006 was observed to be marine and from the 'baseline' sector of the Cape Grim wind profile, as shown by a back trajectory (Fig. 4).

Methyl iodide concentration in seawater was highest near the rocky reef, with a rapid decrease moving away from the coast measured in each transect down to a level of 11.4 ± 1.3 pM at 5-km offshore (Fig. 5). Phytoplankton biomass as measured by chlorophyll a (Chl a) was generally lower and more variable at the inshore location (0.33 ± 0.17 μg of Chl a) and was greater and less variable in the offshore sites, up to 0.6 ± 0.08 μg of Chl a at 5 km (Fig. 5). Stress on phytoplankton, indicated by a reduced maximum quantum yield of photosystem II was greatest at the inshore site (Fig. 5). The phytoplankton community contained diatoms, dinoflagellates, chlorophytes, coccolithophores and *Phaeocystis* sp. Inshore waters were depleted in nitrogen compared with offshore waters; the total nitrogen ranged from $(0.11 \pm 0.07) \times 10^{-6}$ M near the shore, compared with $(0.59 \pm 0.1) \times 10^{-6}$ M at 100-m offshore or greater (Fig. 5). Phosphorus was not similarly depleted, which resulted in an N : P ratio of 0.4 ± 0.2 inshore and 2.0 ± 0.5 offshore.

Small particles in the 3–10-nm range, referred to as ultrafine condensation nuclei (UFCN) were continuously monitored at the Cape Grim BAPS.[19] The only occasions when UFCN were detected at the station in air of clean, marine origin ('baseline' air) were on the afternoon of 11 February 2006 with a count of maximum 3720 cm^{-3} and counts of < 1000 cm^{-3} on 4 and 5 February 2006 (Figs 2 and 3). No events where small particles grew from the UFCN (3–10 nm) range to the CCN (>30 nm) size were observed during the campaign.[19] High concentrations of UFCN were measured at the station during periods when air was from a terrestrial origin ('non-baseline'), which included air from a local bushfire.[21]

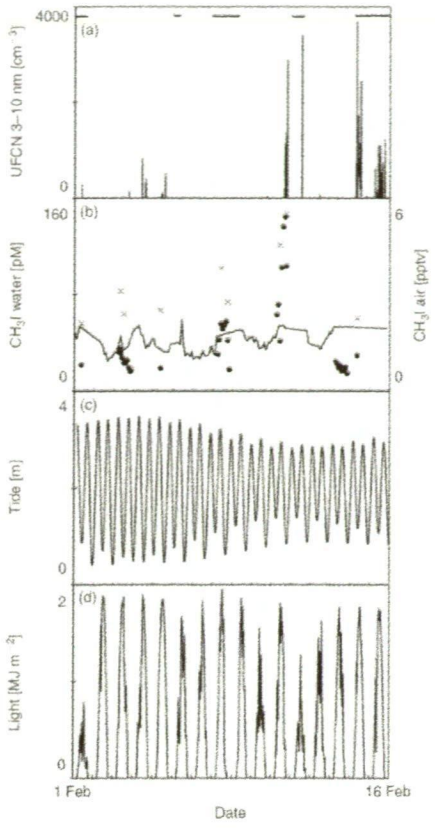

Fig. 2. 1–16 February 2006, Cape Grim BAPS. (a) UFCN (particles 3–10 nm) measured at station (bars), wind from 'non-baseline' sectors shown by horizontal lines; (b) methyl iodide concentration in inshore seawater (circles), in air at sea level (crosses), and in air at the station (line); (c) tide height; and (d) light level.

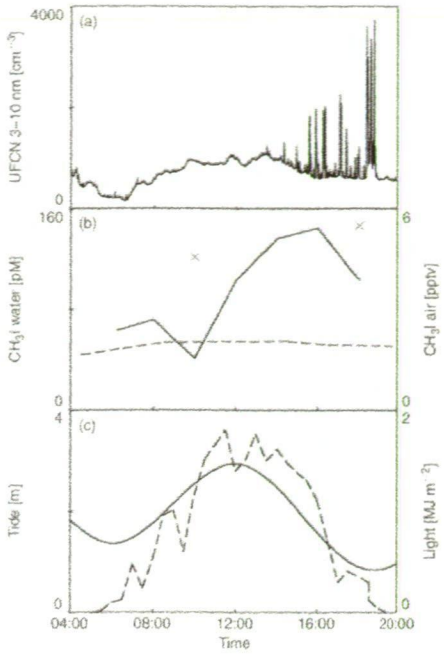

Fig. 3. 11 February 2006, Cape Grim BAPS. (a) UFCN (particles 3–10 nm) measured at the station; (b) methyl iodide concentration in inshore seawater (line), in air at sea level (crosses), and in air at station (dashed); (c) tide height (line), and light level (dashed).

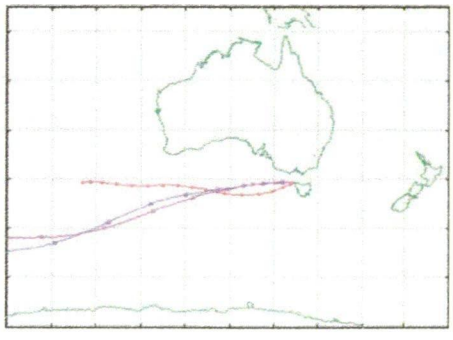

Fig. 4. Back trajectory of air mass arriving at Cape Grim BAPS on 11 February 2006. Data points were taken every 6 h, back to 96 h, at three air pressures (diamonds 1000 hPa, squares 700 hPa, crosses 550 hPa).

Discussion

Methyl iodide concentration was much greater nearest the rocky reef, and fell away rapidly from the coast (log relationship of $y = -5.5\ \mathrm{Ln}(x) + 56.5$, $R^2 = 0.95$) (Fig. 4). Methyl iodide concentration was also not strongly correlated with phytoplankton biomass. Both these findings suggest that the inshore environment and kelp beds are a far larger source of biogenic methyl iodide than the phytoplankton in seawater. Phytoplankton at the inshore site were under some stress as indicated by a low maximum quantum yield of photosystem II, which may have initiated methyl iodide production. However, the magnitude of emission is greater than that from phytoplankton communities at this level of biomass, even when under stress.[12–14]

The flux of methyl iodide was determined, as described by Richter,[22] for inshore and offshore conditions, where a pair of methyl iodide measurements were made in the surface water and in the air above that water. The mean inshore flux was $12.8 \pm 8.9\ \mathrm{nmol\ m^{-2}\ day^{-1}}$, and flux at 5-km offshore was $3.4 \pm 1.6\ \mathrm{nmol\ m^{-2}\ day^{-1}}$. While all waters around Cape Grim showed a sea-to-air flux of methyl iodide, inshore waters

provided a consistently stronger source of methyl iodide to the atmosphere than offshore waters. On 11 February, the inshore flux was 98.6 nmol m^{-2} day^{-1}, which is nearly eight times the mean flux at the same location on other days during the same period.

Methyl iodide concentration in air measured at Cape Grim BAPS (on top of a 94-m cliff) was 1.5 ± 0.3 parts per trillion (ppt), which is within the range previously found of 1.9 ± 0.5 ppt[23] and 1.62 ± 0.93 ppt[24] in 'baseline' air during summer, and did not show a peak on 11 February 2006 (Fig. 2). At sea level, the concentration in air was 3.21 ± 1.2 ppt with a peak of 5.5 ppt on 11 February 2006, which suggests that the inshore methyl iodide source is localised and is largely dispersed before reaching the station. This finding is consistent with other findings of enrichment of methyl iodide immediately over seaweed beds.[25–27]

The main intertidal kelp species on the rocky reef is Bull Kelp (*Durvillaea potatorum*), which is present in an exceptionally high biomass, in the upper range of values observed for other species of brown algae.[15] However, the limited extent and steep topography of the reef at this location, combined with a small tidal range means that only a limited kelp biomass is exposed at low tide. Compounding this, *D. potatorum* contains in the order of 90 mg per kg of iodine,[17] compared with as much as 50 000 mg kg^{-1} in *Laminaria digitata*.[18] The large amounts of rotting beach-cast kelp at the north end of the beach nearest the station (63 kg m^{-2}) may be responsible for significant emissions directly to the atmosphere. However, the data collected here suggests that living kelp also produce periodic strong emissions of methyl iodide.

The data also show an apparent relationship between the period of elevated methyl iodide flux from the coast on the afternoon of 11 February and a subsequent period of new particle formation. Air was of marine origin (or 'baseline') at this time (Fig. 5). This provides indirect evidence that production of methyl iodide from an inshore marine origin is linked to a particle formation pathway during this time.

The atmospheric lifetime of methyl iodide at this latitude in summer has been estimated as 4–5 days.[23] This means that the emission of methyl iodide in coastal waters did not directly act as a precursor to new particle formation in this instance, as the methyl iodide emitted at the coast would not be broken down into iodine until far from the station vicinity. However, the data do suggest that the emission of methyl iodide was linked to the particle formation pathway, and perhaps has a common cause.

The emission of methyl iodide may have been coincident with emission of other gases that acted as precursors to new particle formation. Direct emission of I_2 from macroalgae is suspected to provide a major mechanism for particle formation at Mace Head,[10,11,16] and the Bull Kelp, *Durvillaea potatorum*, has been shown to directly emit moderate levels of iodine as I_2.[19] Unfortunately, I_2 emitted directly from kelp was not measured in the field concurrent with methyl iodide, and so its significance in this case is unknown. It is possible that elevated emission of methyl iodide was associated with a period of I_2 emission and this provided a precursor to particle formation. Another possibility is that the period of elevated methyl iodide production was concurrent with direct emission of particles that contain aromatic compounds from the kelp, as shown in a chamber experiment also completed during the campaign.[19] A scenario such as this is supported by previous measurements at Cape Grim, which indicated particle concentrations were high when the odours from kelp rose to the station in calm sunny conditions,

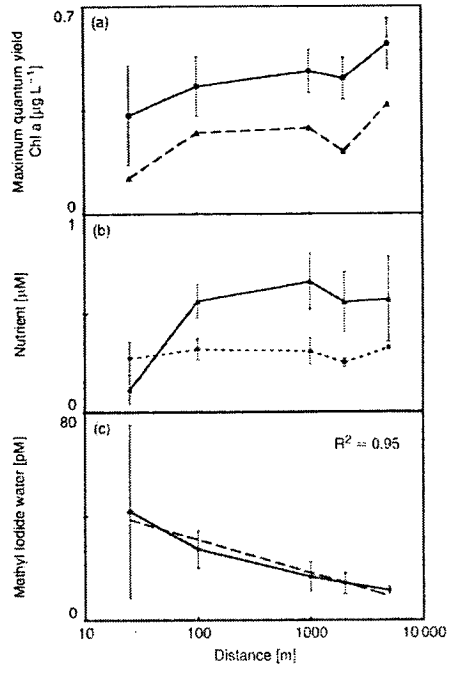

Fig. 5. Combined and averaged data from inshore and transects, February 2006, Cape Grim BAPS. Note log scale. (a) average chlorophyll a fluorescence of seawater at each station (line) and average maximum quantum yield of phytoplankton (dashed line); (b) average total nitrogen (line) and phosphate (dashed line) concentrations in seawater at each station; (c) average methyl iodide concentration in seawater at each station (solid line), fitted log trend line (dashed).

and that the odour and particles had a common source at the coast.[28]

The concentrations of another gas that can act as a precursor to particle formation, dimethyl sulfide (DMS) did not show a corresponding peak during the period of new particle formation[21] and does not appear to be involved in particle formation processes in this instance. Measurements of the alkyl halides CH_2I_2, CH_2IBr, and CH_2ClI have been previously measured to be below detection limits (~0.04 ppt) at Cape Grim, unlike at Mace Head.[29] Assuming this was the case during the study period, these alkyl halides did not contribute to the particle formation pathway.

The maximum count of small particles during this period was 3720 cm^{-3}, which is small compared with a typical burst of new particles from a coastal source at Mace Head of 598 900 cm^{-3}.[30] Also, particle growth from the 3–10 nm size range to the >30 nm size and further into CCN-sized particles was not observed to be associated with this event.[19] There was no regular and predictable detection of new particles associated with low tide, as was found at Mace Head.[30]

The cause of the period of elevated methyl iodide is not clear. Methyl iodide peaked during receding tide and afternoon sun,

which infers some degree of photo-oxidative stress to the kelp. However, the peak in methyl iodide began in the middle of the day when the tide was high, and the detection of new particles that followed the peak in methyl iodide occurred between 1600 and 1900 hours, when light was fading. In addition, there was no regular and predictable pattern of methyl iodide emissions associated with low tide on each day, with only one incident of elevated methyl iodide found. Low nitrogen concentration and N : P ratio (Fig. 5), along with low quantum yield of photosystem II in phytoplankton at the inshore site suggests phytoplankton in the inshore environment experience nutrient depletion and stress, which may also be experienced by the kelp. However, the conditions during this period were not exceptional, and similar levels of stress would be present on other days.

Conclusions

The data show a consistently positive ocean-to-atmosphere flux of methyl iodide, which indicates that the inshore environment at this location is consistently a source to the atmosphere. The pattern of methyl iodide flux suggests that the coast, where a rocky reef that contains beds of Bull Kelp is located, is a stronger source of methyl iodide than the phytoplankton community. There are periodic pulses in the source where methyl iodide emission is elevated, and this elevated flux was concurrent with detection of new small particles on one sampling day. Methyl iodide did not act as a precursor to new particles, but the peak in methyl iodide emission is likely to have been simultaneous with a high flux of other unmeasured gases that acted as precursors to new particle formation. The cause of this event is not clear, however photo-oxidative and nutrient stresses were likely to be present.

Several factors suggest that the emission of I_2 or iodinated gases by kelp are less important contributors to bursts of new particles that can then grow into viable CCN for cloud formation in this region compared with Mace Head. First, there were no regular and predictable bursts of new particles at every low tide and full sun as is found at Mace Head during summer.[30] Second, the one measurement of new particle concentration during baseline conditions was low compared with other locations, and failed to undergo growth into CCN. It appears that following particle nucleation, the subsequent mechanisms of particle growth were not present or not strong enough to create CCN. However, it appears that a minor particle formation pathway present in the inshore environment is associated with a high methyl iodide emission.

Methods

Water and air samples were collected between 1 February 2006 and 16 February 2006 by two main strategies: (1) 4 days of sampling near kelp beds at 0.5-m depth via a moored 60-m poly(propylene) pipe and a diaphragm hand pump from 0600 until 2000 hours Eastern Australian Daylight Savings Time, and (2) three transects from a small boat along a transect line away from the coast (sites at 0.1, 1, 2, and 5-km offshore). At this location for this period sunrise was at ~0640, local midday at 1330, and sunset at 2030 hours. Sampling sites and location of kelp beds are shown in Fig. 1.

Water samples were collected and analysed as follows: 5 mL were used for immediate analysis of maximum quantum yield of photosystem II by pulsed amplitude-modulated (PAM) fluorometer analysis (WALZ water PAM). One litre of seawater was filtered onto 47-mm GF/F filters within 2 h of sampling and stored frozen in the dark until analysis for Chl a by methanol extraction and Turner fluorimetry.[31] One litre of seawater was preserved with 1 mL of Lugol's iodine solution and stored in the fridge before examination by inverted microscopy. Two 10-mL samples of seawater in polycarbonate tubes were stored frozen in the dark until analysis for macronutrients (nitrate, nitrite, phosphate, and silicate) by autoanalyser within three months of sampling.

Methyl iodide concentrations in air and water were measured using purge and cryotrap gas chromatography with electron capture detection within a few hours using the equipment and methods described in Sturrock et al.[32] Water samples were collected in 100-mL glass syringes, air samples collected in evacuated, glass-lined stainless-steel flasks using a battery powered pump.

To assess Bull Kelp biomass, 80 plants over a 14-m length of reef were collected and weighed. Plant density was recorded in 221 × 1 m^2 quadrants of at random sites on the reef. Biomass of beach-cast kelp was assessed using 1 × 1 m^2 quadrants randomly allocated in a two-tiered sampling system (high and low biomass areas).

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Appendix 2. Cainey et al. 2007a

RESEARCH FRONT

Highlight

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J. M. Cainey et al., *Environ. Chem.* 2007, *4*, 151–154. doi:10.1071/EN07006

Flux chamber study of particle formation from *Durvillaea potatorum*

Jill M. Cainey,[A,E] *Melita Keywood,*[B] *E. Keith Bigg,*[C] *Michael R. Grose,*[D] *Rob W. Gillett*[B] *and Mick Meyer*[B]

[A]Cape Grim Baseline Air Pollution Station, Bureau of Meteorology, 159 Nelson Street, Smithton, Tas. 7330, Australia.

[B]CSIRO Marine and Atmospheric Research, Aspendale, Vic. 3195, Australia.

[C]Castle Hill, NSW 2154, Australia.

[D]IASOS, University of Tasmania, Hobart, Tas. 7001, Australia.

[E]Corresponding author. Email: j.cainey@bom.gov.au

Environmental context. Kelp at Mace Head, Ireland, produces large quantities of iodine when exposed to sunlight at low tide and this iodine results in the rapid production of particles. Cape Grim, Tasmania, also has large colonies of kelp (*Durvillaea potatorum*) but its role in particle formation appears limited. A flux chamber was used to better understand the response of *Durvillaea potatorum* to light stress and ozone.

Abstract. Brown kelp, in particular *Laminaria digitata* at Mace Head, Ireland, has been shown to emit iodine when under stress, resulting in new particle formation. The Cape Grim Baseline Air Pollution Station, Tasmania, is surrounded by rocky reefs that support large colonies of the brown kelp *Durvillaea potatorum*. During an intensive campaign in February 2006 at Cape Grim, levels of IO, OIO and methyl iodide remained at background levels and no particle formation events could be associated with locally generated precursor iodine species.

In order to better understand the limitations of the local kelp to provide a source of precursor species, samples of *Durvillaea potatorum* were collected from the beach below the Cape Grim Station and tested for their capacity to initiate particle formation using a flux chamber technique. Particles were observed only when the kelp was exposed to both very high levels (>100 ppb) of ozone and natural solar radiation. There was a high correlation between ozone level and particles produced. The particles resulting from exposure to high levels of ozone were aromatic and volatile.

Durvillaea potatorum appears to plays a very limited role in contributing to particle formation at Cape Grim, but it does represent a source of atmospheric iodine under photo-oxidative stress, of 18 pmol g^{-1} (fresh weight) min^{-1} and is likely to have a significant role in atmospheric chemistry at this site.

The role of the brown kelp, *Laminaria digitata*, in providing the necessary precursors to nucleation events at Mace Head, Ireland, has been well studied,[1–3] and it had been expected that the brown kelp, *Durvillaea potatorum*, at Cape Grim, Australia, would also provide a source of iodine and iodated gases that would initiate particle formation.

Previous measurements at the Cape Grim Baseline Air Pollution Station of a range of alkyl halides, including IO and OIO, had shown that these gases were either at low levels or below detection limits,[4–6] and this was suggested to be the result of the distance of the Cape Grim Station from the source region on the beach 94 m below.[7] Measurements of particle numbers, both at the Station and on the beach below had previously shown that beach cast *Durvillaea potatorum* was a source of particles[8,9] and at the same magnitude as observed at Mace Head, 20 000 and 57 000 respectively.[1,9]

During the Precursors to Particles Campaign 2006 (P2P 2006),[10] the expected nucleation events due to the local macroalgae, *Durvillaea potatorum*, were not observed, suggesting differences between the processes at Cape Grim and at Mace Head. Initial tests during P2P 2006 showed that beach cast *Durvillaea potatorum* produced particles only when exposed to high levels of ozone (>450 ppb) and light. To better understand the possible role of the local kelp as a source of particles, a limited assessment of *Durvillaea potatorum* was made using a flux chamber, in an approach similar to that used by Palmer et al.[11]

Bull Kelp, *Durvillaea potatorum*, was collected from the beach 94 m below the Cape Grim Baseline Air Pollution Station by cutting a frond from a rocky outcrop at high tide to minimise stress and it was stored in seawater before use in the flux chamber.

The kelp (3.15 kg fresh wet weight) was placed in a 250-L flux chamber, with mylar walls, transparent to UV-B radiation.[12] The flux chamber was sited on a bench on the Cape Grim instrument deck. The flux chamber also contained an ozone generator (Rollex HV-206A, New Zealand) and the ozone concentrations and particle number concentrations were monitored continuously. Ozone concentration in the chamber was measured using an ozone calibrator (ML9811, Monitor Laboratories, USA). Particle number concentrations were measured using a TSI 3776 CPC (TSI Corporation, USA), which was connected to the flux chamber using a short (<1 m) length of antistatic tubing to minimise particle loss.

The flux chamber was not leak tight and to ensure that ambient air did not enter the chamber a small diaphragm pump (Dynavac OD1, Australia) was used to provide airflow at 12 L min^{-1} to maintain the chamber at a positive pressure. A HEPA filter (Pall Gelman #12144, USA) was fitted to the outlet of the

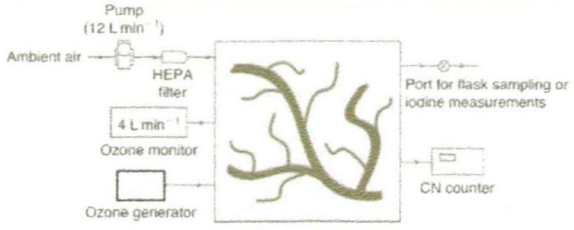

Fig. 1. Schematic diagram of the experimental set-up of the flux chamber for the December 2006 work. The ozone monitor was not included during the P2P 2006 study in February 2006.

Table 1. Provides the running period of the ozone generator, the peak ozone concentration achieved in the flux chamber for that period generation and the resulting peak particle number concentration in the chamber, for the measurements performed in December 2006 on *Durvillaea potatorum*

Rollex ozone generator [s]	Peak ozone [ppbv]	Peak particles [N cm^{-3}]
10	117	2.81×10^3
15	122	2.15×10^3
20	136	1.19×10^4
30	247	6.08×10^4
40	314	1.64×10^5
60	390	3.34×10^5
90	439	4.18×10^5
120	455	5.04×10^5

pump to remove any particles. This flow of particle-free air also flushed the chamber between each change in ozone level. The experimental set up is shown in Fig. 1.

The ozone generator was turned on for a specified period (see Table 1) and then turned off. Particle numbers showed an immediate response to the addition of ozone and the concentration of both was allowed to increase and then decay back to ambient levels before restarting the generator (Fig. 2).

Iodine measurements could not be made on the flux chamber simultaneously due to the high levels of water vapour in the chamber, which contaminated the trap measurements. However a small 1-L chamber was used to assess the iodine emissions from subsamples of *Durvillaea potatorum*, when exposed to ambient light, using an ethanol trap as described by Palmer et al.[11] but with the addition of an ice and sodium chloride (−15°C) water trap in line between the chamber and the ethanol sparger. The blank for iodine was assessed by determining the iodine emissions from the empty 1-L flask, which demonstrated that there was no iodine without the presence of kelp. Measurements were made on several fresh strands of kelp ($n = 9$) and iodine emissions from kelp exposed to ambient sunlight were 18 ± 11 pmol g^{-1} (FW) min^{-1}.

During P2P 2006, as part of the initial trials, six transmission electron microscopy grids were placed in the chamber, immediately before exposure to ~450 ppb of ozone, and left for 24 h. It was expected that very large numbers of the small newly formed particles would be collected on the grids; however, an untreated grid was apparently devoid of particles when examined, while those exposed to decane, decanol, or dimethylsulfoxide vapours showed only a few. Only the grid exposed to xylene vapour showed many particles like that of Fig. 3. This suggests that the particles evaporated before they could be examined in the electron microscope unless previously stabilised by dissolving in xylene.

An aromatic is perhaps the most common class of compound that would be readily soluble in xylene but not in decane, decanol or dimethylsulfoxide vapours. Some of the crystals formed exceeded 1 μm in length but had widths <200 nm and their thickness, while indeterminate, appeared to be much lower. Growth of airborne particles in a small chamber to a size large enough to create such crystals is very improbable. Instead, a deposit of fine droplets on the collecting surface, which coagulated to form larger drops, is indicated. The fact that the large drops were not observed in the electron microscope unless stabilised by xylene suggests a compound with a relatively high vapour pressure, which includes some organics and aromatic compounds. The atmospheric lifetime of very small, nucleated particles of this material would, therefore, probably be short when the gas from which they formed became subsaturated, even if they were to be nucleated in the presence of ambient ozone conditions.

The results from the flux chamber in December 2006 show a very strong relationship between ozone added and particle production from *Durvillaea potatorum*, with an exponential fit giving an R^2 of 0.93 (Fig. 4). If this fit is used to extrapolate back to ambient ozone levels at Cape Grim, it implies that between 900 and 1300 N cm^{-3} can result from the interaction of the kelp and ozone. The ambient ozone concentration during P2P 2006 and in December 2006 was 15–16 ppb, suggesting that ambient particle generation would be at the lower end of the predicted range and in agreement with the particle number concentrations measured on the beach, directly over beach cast *Durvillaea potatorum* of 843 ± 205 N cm^{-3}.[10]

The response of *Laminaria digitata* to a variety of ozone levels varied markedly between samples of the kelp,[11] with particle numbers reaching 650 N cm^{-3} with 500 ppb of ozone, but also showing little or no response to subsequent additions of ozone at 500 ppb (see fig. 8, Palmer et al.[11]). In their fig. 8, *Laminaria digitata* produced >275 000 particles with only the addition of 280 ppb of ozone. For one sample of *Laminaria digitata*, there was a strong relationship (R^2 of 1) between ozone added and particle number generated.[11] These points are shown here in Fig. 4 and clearly *Laminaria digitata* produces significant numbers of particles at much lower levels of ozone than *Durvillaea potatorum*.

Flux chamber study of particle formation from *Durvillaea potatorum*

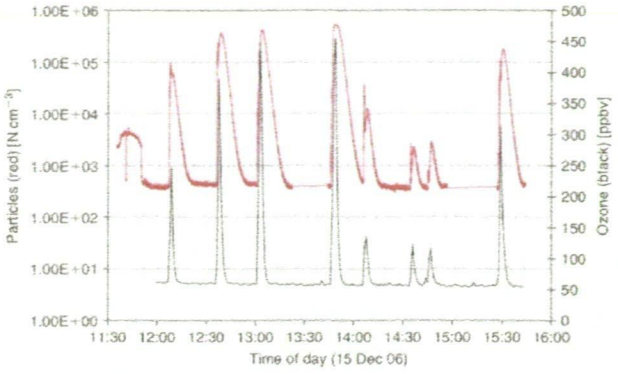

Fig. 2. Shows the response of fresh *Durvillaea potatorum*, in terms of particle numbers, to elevated levels of ozone, during the December 2006 flux chamber work.

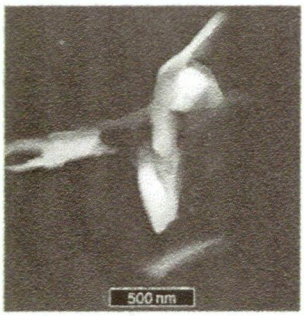

Fig. 3. Shows a particle collected in xylene resulting from the exposure of *Durvillaea potatorum* to ~450 ppb of ozone during the flux chamber work performed as part of P2P 2006 (February 2006).

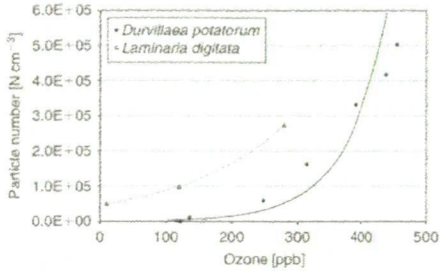

Fig. 4. Shows the relationship between peak ozone exposure and peak particles produced for both *Durvillaea potatorum* and *Laminaria digitata*.[11]

Ambient levels of ozone at Cape Grim range seasonally between 15 ppbv in summer and 30 ppbv in winter,[13] so the levels used in the flux chamber experiment are not likely to occur in the clean marine boundary layer. The lowest level of ozone achieved in the flux chamber was close to 100 ppb and this was at the limit of controlling the operation of the generator.

While the kelp beds 94 m below the Cape Grim Station contain a much higher biomass than the beds at Mace Head, 82 kg m^{-2} and 2.5 kg m^{-2} respectively,[14,15] *Durvillaea potatorum* has a far lower iodine content than *Laminaria digitata*. Preliminary measurements indicate that it contains in the order of 90 mg kg^{-1} of iodine[16] compared with *Laminaria digitata*, which contains 2500–12 000 mg kg^{-1}.[17]

In contrast to the iodine content of the kelp, the emission of iodine from *Durvillaea potatorum* at 18 pmol g^{-1} (FW) min^{-1} is consistent with emissions from unstressed or mildly stressed *Laminaria digitata*, which emitted iodine in the range 3–130 pmol g^{-1} (FW) min^{-1}.[11] This suggests that the kelp at Cape Grim still represents a potential source of iodine given its high biomass and iodine emissions under moderate photo-oxidative stress.

Durvillaea potatorum is not likely to be a major source of new particles at Cape Grim, but could represent an important source of iodine, which may induce limited particle formation and also contribute to the iodine in aged aerosols. Emissions of iodine and iodated species, including methyl iodide, from *Durvillaea potatorum* are likely to have an important role in atmospheric chemistry at Cape Grim[15,18] and iodine has previously been measured in individual particles at Cape Grim.[19]

Further work at Cape Grim is needed to extend the limited study reported here by assessing other types of macroalgae found locally at Cape Grim for their potential to produce the precursor gases needed for particle generation and the robustness of the relationship between particles produced and ozone concentration. In addition, a range of precursor gases should be continuously monitored, along with particle numbers, to better determine the identity of any precursors to particle formation.

A campaign is planned at Cape Grim for late 2007 (Austral spring/summer) to address the points above.

Coastal regions and the open ocean support high biological activity and occupy a large surface area.[20] If the processes that are important at Mace Head, where the local biology (*Laminaria digitata*) provides nucleating precursors to particles, are also important in Tasmania then these regions are likely to be highly critical for particle production and the understanding of particle production. However, the specific conditions and coastal ecology of the ocean near Tasmania are very different to the environment of the Northern Hemisphere coastlines and oceans. The assessment of the local kelp, *Durvillaea potatorum*, at Cape Grim suggests that while it may contribute to new particle numbers it does so at close to three orders of magnitude lower than that observed for *Laminaria digitata* at Mace Head. Clearly, further work is needed to assess a range of macroalgae along a variety of coastlines, in a variety of conditions, before the processes observed at Mace Head can be assumed to be applicable globally.[21]

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Appendix 3. Cainey et al. 2007b

RESEARCH FRONT

Overview

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J. M. Cainey et al., *Environ. Chem.* 2007, *4*, 143–150. doi:10.1071/EN07041

Precursors to Particles (P2P) at Cape Grim 2006: campaign overview

Jill M. Cainey,[A,I] *Melita Keywood,*[B] *Michael R. Grose,*[C] *Paul Krummel,*[B] *Ian E. Galbally,*[B] *Paul Johnston,*[D] *Rob W. Gillett,*[B] *Mick Meyer,*[B] *Paul Fraser,*[B] *Paul Steele,*[B] *Mike Harvey,*[E] *Karin Kreher,*[D] *Torsten Stein,*[F] *Ossama Ibrahim,*[F] *Zoran D. Ristovski,*[G] *Graham Johnson,*[G] *Cathie A. Fletcher,*[G] *E. Keith Bigg*[H] *and John L. Gras*[B]

[A]Cape Grim Baseline Air Pollution Station, Bureau of Meteorology, 159 Nelson Street, Smithton, Tas. 7330, Australia.

[B]CSIRO Marine and Atmospheric Research, Aspendale, Vic. 3195, Australia.

[C]Institute of Antarctic and Southern Ocean Studies, University of Tasmania, Hobart, Tas. 7001, Australia.

[D]National Institute of Water and Atmospheric Research, Lauder, New Zealand.

[E]National Institute of Water and Atmospheric Research, Greta Point, Wellington, New Zealand.

[F]Institute of Environmental Physics, University of Heidelberg, Heidelberg D-69120, Germany.

[G]ILAQH, Queensland University of Technology, Brisbane, Qld 4001, Australia.

[H]Castle Hill, NSW 2154, Australia.

[I]Corresponding author. Email: j.cainey@bom.gov.au

Environmental context. Understanding the role of clouds in assessing the impact of climate change is a challenging issue. It is thought that plankton and seaweed contribute to the formation of clouds by emitting gases that lead to the particle production necessary for cloud formation. Macroalgae (kelp) at Mace Head, Ireland, produce large quantities of iodine when exposed to sunlight at low tide and this iodine results in the rapid production of particles. Cape Grim, Tasmania, also has large colonies of kelp and the role of Bull Kelp (*Durvillaea potatorum*) in particle production was assessed.

Abstract. Iodine emissions from coastal macroalgae have been found to be important initiators for nucleation events at Mace Head, Ireland. The source of this iodine is the large beds of the brown kelp *Laminaria digitata*, which are significantly exposed at low tide.

On the coast around Cape Grim, Tasmania, there are beds of the brown kelp *Durvillaea potatorum*. The Precursors to Particles 2006 (P2P 2006) campaign at the Cape Grim Baseline Air Pollution Station in late summer (February) 2006 focused on the role of this local kelp in providing precursor gases to particle formation.

Durvillaea potatorum does not produce iodated precursor gases at the levels observed at Mace Head. IO was measured at 0.5 ± 0.3 ppt, while OIO was below detection limits (9 ppt). The dominant atmospheric iodated species was methyl iodide and the average concentration measured at the Cape Grim Station was 1.5 ± 0.3 pptv in baseline conditions, but showed significant variation in discrete samples collected immediately above the ocean surface.

Nucleation events were not detected at the Cape Grim Station, except for one period where the plume of a local bushfire interacted with air of marine origin. The passage of four fronts did not result in nucleation bursts and measurements on the beach 94 m below the Cape Grim Station suggested that *Durvillaea potatorum* was only a weak source of new particles.

Additional keywords: iodine, kelp, methyl iodide, particle formation.

Introduction

Coastal macroalgae have been shown to be important emitters of gases which initiate nucleation events. Such events are frequently observed during daylight at Mace Head, Ireland, and often coincide with low tide and the period around solar noon and maximum radiation levels. The major source of these nucleating species at Mace Head is the large beds of the brown kelp *Laminaria digitata* immediately off the beach at the monitoring station exposed at low tide.[1,2]

Secondary organic aerosol formation at Mace Head has been well studied,[1,3,4] and CH_2I_2 was found to be present at significant levels with other alkyl halides at much lower levels.[5] Although CH_2I_2 was initially thought to provide the precursor to the IO required to initiate nucleation events,[5] iodine emissions are now deemed more critical for particle formation, as they can more readily react in the atmosphere to give the IO. It is clear that *Laminaria digitata* has a significant role in providing the necessary precursor gases for these events.[6]

However, work at other sites has been limited and has not been extended to other kelps. There are *Laminaria digitata* beds off the north-western coast of Europe, which emit significant quantities of iodine and iodated species;[7,8] however, particle formation at these sites has not been assessed. Any attempt to extrapolate measurements, made only at Mace Head and in

waters containing *Laminaria* kelps, to coastal regions globally can only be speculative[9] and is likely to give an inaccurate estimate of global importance.

In the first published report of the Cape Grim station,[10] it was noted that on the relatively rare occasions of calm sunny days in winter and spring, particle concentrations would sometimes exceed 20 000 N cm^{-3} and were accompanied by the odour of rotting kelp. Bigg and Turvey[11] used a portable counter to show that the source of the particles was piles of kelp on the beach below Cape Grim, and was dependent on the kelp being in the sun. The occurrence of such events only on calm sunny days in winter and spring implies a photochemical production, since background particle surface area will then be at a minimum. It also implies a relatively weak source that only leads to particle production under these special conditions.

To expand the work on iodine emitted from macroalgae as a precursor to particle formation, and to examine a location other than Mace Head, a 4-week Surface Ocean Lower Atmosphere Study endorsed campaign, Precursors to Particles 2006 (P2P 2006), ran from 30 January to 24 February in 2006. P2P 2006 focused on biology, precursor gas and particle measurements at the Cape Grim Baseline Air Pollution Station, Tasmania, Australia.

The aims of P2P 2006 were to identify and quantify the gaseous precursors involved in new particle formation at Cape Grim. Nucleation events would be identified by continuously measuring microphysical properties of the aerosol such as particle number concentration, particle size distribution, the hygroscopic growth and volatility of nanoparticles, and size-resolved chemical composition of particles. These continuous particle measurements would then be compared with the continuous measurements of implicated precursor gaseous species for new particle formation, such as IO, OIO, DMS and CH_3I.

Measurements of particle numbers were also made on the beach 94 m below the Cape Grim station, along with discrete sampling of air samples to identify any precursor gases, for a comparison with the data collected at the station above. The beach work was also combined with regular boat trips along the 5-km, 270° transect at Cape Grim to monitor micro- and macroalgae and surface concentrations of methyl halides in surface waters and immediately above the surface water. The local brown kelp *Durvillaea potatorum* was also assessed for iodine emissions and particle formation using a flux chamber.

This paper provides an overview of the P2P 2006 campaign and the other papers in this Research Front provide the details of the specific measurements made. Bigg[12] reports on the transmission electron microscopy (TEM) assessment of particles at Cape Grim, while Fletcher et al.[13] report the results of measurements made using a volatility hygroscopicity tandem differential mobility analyser (VH-TDMA). Measurements of oxygenated volatile organic gases by Galbally et al.[14] indicate that the levels of these gases at Cape Grim are significantly lower than observed in the Northern Hemisphere. Grose et al.[15] focus on the micro- and macroalgae at Cape Grim and on CH_3I, while the assessment of the dominant macroalgae, *Durvillaea potatorum* by Cainey et al.[16] gave insights into the limited role the local kelp has on new particle formation.

Precursors to Particles 2006 (P2P 2006)

The Cape Grim Baseline Air Pollution Station is located on the north-west coast of Tasmania (40°40′56″S, 144°41′18″E). The station is part of the Global Atmosphere Watch program and has been in continuous operation since April 1976. The station is situated at the top of 94 m cliffs and is surrounded by a rocky reef that supports a variety of macroalgae. The dominant intertidal kelp species is Bull Kelp (*Durvillaea potatorum*), which is found in high density. At low tide, it is partially exposed to the atmosphere and UV radiation. In addition to the large biomass of living kelp on the rocky reef, there is also a large biomass of beach-cast kelp on Valley Bay Beach below the Cape Grim Station (Fig. 1), dominated by Bull Kelp.

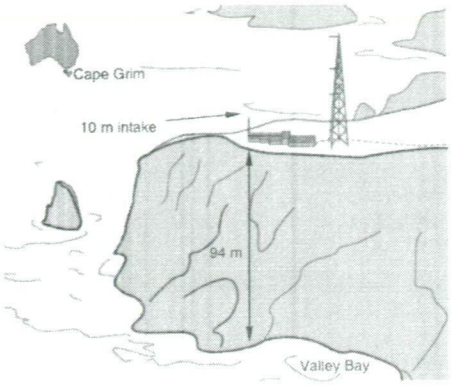

Fig. 1. Location of Cape Grim and the location of the Station in relation to the beach below.

Cape Grim is located in the 'roaring 40s' and experiences clean onshore winds, 'baseline conditions', for 30–40% of the year. Baseline conditions are defined as air masses that arrive at the station in the sector 190–280° and that meet a strict seasonally varying condensation nuclei (CN) number concentration criteria. The CN criteria ranges between 350 N cm^{-3} in winter and 1500 N cm^{-3} in summer to take account of the natural cycle in CN numbers. Baseline air originates over the Southern Ocean and has had no significant contact with land.

Physical conditions during the campaign (light intensity, tide, wind direction and periods of 'baseline' air) are shown in Fig. 2. The campaign was characterised by significant periods of baseline conditions (clean onshore winds), with reasonably clear conditions throughout. The ceilometer (CT25K, Vaisala, Finland) at Cape Grim gave an average cloud coverage of 51 ± 17%. There were four fronts, with only the front on the 9 February bringing any significant rain (9.8 mm). When conditions were suitable, 0000Z radio-sonde (Digicora MkI, MW11, Vaisala, Finland) flights to a height of 8 km were flown to determine the structure of the lower atmosphere. The boundary layer height ranged between 400 and 1980 m, with an average height of 1233 m.

Precursor gases

Potential iodated precursor species measurements were made by National Institute of Water and Atmospheric Research from the deck at the Station for IO using a multiple axis differential optical absorption spectrometer (MAX-DOAS).[17,18] Two further MAX-DOAS instruments, from the University of Heidelberg, operated to detect IO and OIO, both on the deck at the Station and on the beach 94 m below the station. These measurements

Overview of the P2P campaign

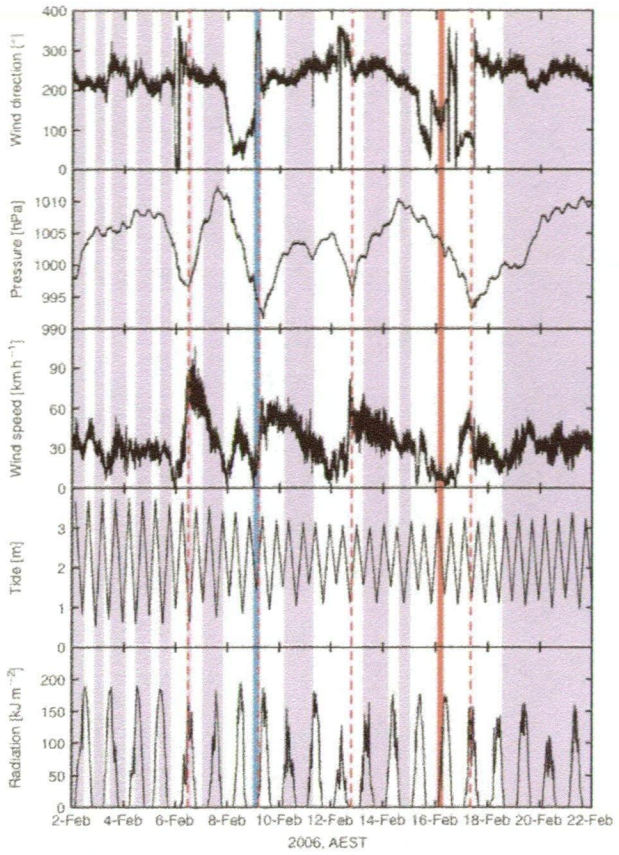

Fig. 2. Summary of the general conditions during P2P 2006. Purple shading represents extended periods of baseline conditions; red dashed line represents the passage of a front; blue shading represents significant rainfall (>0.2 mm); and orange shading represents the period affected by the bushfire plume.

indicated that OIO was below detection limits (9 pptv) and that IO ranged between 0.2 and 0.5 pptv throughout the campaign.[19] Previous measurements for IO and OIO at Cape Grim[20,21] suggest that the IO level in onshore winds was 0.4 pptv, compared with 1.2 pptv at Mace Head, and OIO levels reached a maximum after dusk of 3 pptv, compared with 10 pptv at night at Mace Head.[22]

Routine measurements of methyl iodide (CH_3I) were made every 2 h at the Station by the Advanced Global Atmospheric Gases Experiment instruments[23] and flask samples of air from just above the surface of the ocean were collected from the beach and on a 5 km transect off Cape Grim along 270°.[15] CH_3I levels remained close to background (2.1 ± 1.1 pptv) throughout the majority of the campaign. While flask samples collected from immediately above the surface of the ocean did show significant variation from background,[15] these measurements were not frequent enough to resolve short-term periods of significantly elevated concentrations. During the period of the bushfire (16 February), CH_3I levels were significantly elevated (up to 8 pptv); during baseline conditions the concentration was 1.5 ± 0.3 pptv. All CH_3I concentrations are reported on the University of East Anglia (UEA) scale.[5,24,25]

Other alkyl halides, CH_2I_2, CH_2IBr, CH_2ICl, were not assessed during this campaign but have been previously measured at Cape Grim to be below detection limit of 0.04 ppt,[5] in contrast with 0.4 ppt for CH_2I_2 at Mace Head.[26]

A proton transfer reaction mass spectrometer was used during the campaign to monitor volatile organic compounds (VOCs) and oxygenated VOCs.[14] These included isoprene, which has recently been suggested to initiate particle formation[27] and DMS. Isoprene was found to be absent or at very low levels in baseline air,[14] while DMS levels during the

campaign were 66 ± 32 ppt and consistent with previous long-term measurements of DMS made at Cape Grim.[28,29]

Particle measurements

The size distribution of particles was measured with two scanning mobility particle sizers (SMPS), a TSI 3760 (TSI Corporation, USA) measuring between 14 and 700 nm diameter and a TSI nano SMPS (Model 3936, TSI Corporation, USA) measuring between 6 and 150 nm diameter. All measurements were made using the 10-m particle inlet.[30] In addition, an ultrafine condensation nuclei (UFCN) counter (TSI 3025a UFCN) and a CN counter (TSI 3010 CN, TSI Corporation, USA) continuously measured the concentration of particles greater than 10 nm and 3 nm, respectively. The difference between the two particle counters (UFCN-CN; PN3-PN10) was used here as an independent and continuous measurement of new particles.[31] Continuous data for UFCN and CN during the campaign are shown in Fig. 3.

A VH-TDMA operated during P2P 2006 monitoring the volatility and hygroscopic growth of the marine aerosol.[113] For Aitken mode particles, volatilisation mainly occurred in the temperature range ~140–200°C, suggesting the presence of ammonium sulfate or ammonium bisulfate. When Aitken and accumulation mode particles were measured on the same day, the organic content of the Aitken particles tended to be greater than the accumulation particles by roughly 20%. Measurements of the growth factors as a function of relative humidity showed that particles <30 nm deliquesced at around 78.5% (indicating mixtures of ammonium sulfate and non-hygroscopic dicarboxylics), while particles larger than 40 nm showed continuous growth with increasing relative humidity (indicating ammonium bisulfate, sulfuric acid or MSA, or a combination of the three). This indicates that the smaller particles appear to be in a more neutralised state, possibly due to their higher surface-to-volume ratio, allowing them to scavenge any atmospheric ammonia more effectively.[113]

Filter samples for TEM analysis were collected on the beach and at the Station.[112] Particles >500 nm were dominated by sea salt, which were usually coated with exopolymer gels, while particles <300 nm were composed of sulfate and organic material. Particles <50 nm diameter were virus-like and had a morphology consistent with bacteriophage viruses. These primary particles have the potential to act as a nucleating centre for precursor gases.[112]

In addition to the lack of events in the precursor gases, there was little evidence for new particle formation at Cape Grim during P2P 2006. Only the interaction of local bushfire plume with marine air resulted in new particle formation on 16 February. One issue may be the location of the Station inlet 104 m above the beach, leading to a separation of precursor events from particle events.

In an attempt to address this separation of instrumentation from the potential source region, particle measurements were also made on the beach using two different portable counters. The TSI 3007 measures particles larger than 10 nm, while the P-trak measures particles in the range 20–1000 nm. The portable counters were placed close to piles of beach-cast kelp. The kelp was in full sun and clear of the water. The difference between the two instruments was an indication of new particle formation and suggested that the kelp was producing 843 ± 205 N cm^{-3}. This is likely to be an underestimate since it was not possible to measure particle sizes below 10 nm with the portable counters.

However, the particle numbers measured on the beach, either total or new, were below the ambient particle concentration of between 500 and 25 000 N cm^{-3} measured at the station and therefore well within the range of any possible new particle formation measured at the station (0–1200 N cm^{-3}).

There were no unambiguous new particle events either measured at Cape Grim, or using portable counters on the beach, 94 m below the Station. Previous work at Cape Grim[31,32] has suggested that the dominant source of new particles at Cape Grim is the result of post-frontal mixing of free tropospheric air into the marine boundary layer and that the ocean surface represents a significant source of primary aerosol.[112] The passage of four fronts during the campaign did not result in any bursts in nucleation and the only new particles observed were associated with the interaction of the bushfire plume with clean marine air on the 16 February.

Kelp work

Durvillaea potatorum does appear to produce a limited number of new particles; however, given that the beach is 94 m below the station, these particles would rarely be detected by the continuous routine particle measurements made on the 10-m inlet. However, there was coincidence between CH_3I emissions from kelp on the beach and a particle event observed at the station on 11 February.[115]

In an attempt to understand why the processes at Cape Grim appeared markedly different from Mace Head, a limited assessment of the local kelp, *Durvillaea potatorum*, was made. Biomass and plant density was estimated on the reef,[115] as well as emission of iodine.[116] Emission of particles associated with kelp was assessed using a flux chamber[116] in an approach similar to that used by Palmer et al.[133]

The absence of new particle events either at the Station or on the beach suggests that *Durvillaea potatorum* is not likely to be a major source of new particles at Cape Grim, but could represent a significant source of iodine, which could induce limited particle formation and also contribute to the iodine in aged aerosols. Iodine is present in particles at Cape Grim and is associated with organics,[134] indicating that iodine likely derived from kelp is incorporated into the aerosol. Emissions of iodine and iodated species, including CH_3I, from *Durvillaea potatorum* is likely to have an important role in atmospheric chemistry at Cape Grim as even low levels of halogenated gases can have a major impact on the oxidation of other gases.[135]

There are marked differences between Cape Grim and Mace Head, not only in the levels of iodine and iodated species, but in the concentrations of the major atmospheric reactants and the general environment. The species of kelp at each site are different, with widely differing morphology, although *Durvillaea potatorum* emits iodine under stress at rates equivalent to *Laminaria digitata* and is present in far greater biomass. A summary of the two locations in relation to kelp and iodine is given in Table 1.

The average wind speed during P2P 2006 was 8.7 ± 4.1 m s^{-1} and the maximum speed was 29.5 m s^{-1}, associated with the passage of a front on 6 February 2006. During the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) wind speeds ranged from 0.5 to 15 m s^{-1},[136] with a maximum speed of ~28 m s^{-1} (see fig. 2 in Norton et al.[137]).

Cape Grim is dominated by westerly air flow (28%), with baseline wind directions (190–280°) representing 64% of all winds at the site (although not all air masses arriving in this sector would be defined as 'clean'). These air masses typically originate

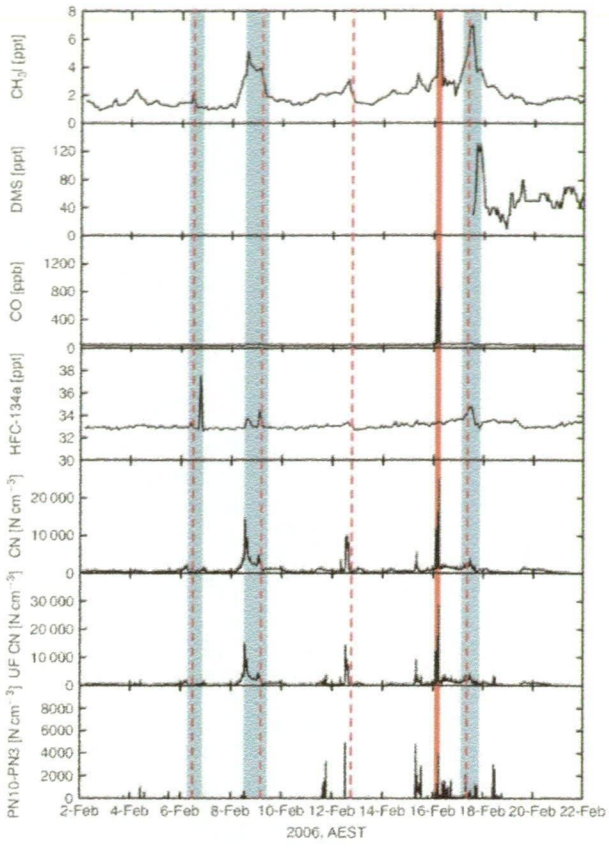

Fig. 3. Precursor gases and particles during P2P 2006, including carbon monoxide as a marker for biomass burning and HFC-134a (CH_2FCF_3) as a marker for air originating from Melbourne. Red dashed lines represent the passage of fronts; grey lines represent periods of Melbourne influence; and orange line represents the bushfire plume.

over the Southern Ocean.[38] Easterlies (21%) and northerlies (15%) represent air masses originating from Tasmania and Melbourne, respectively, with Melbourne air being the most polluted experienced at Cape Grim.[39]

At Mace Head west to north winds (180–300°) dominate, bringing air originating over the North Atlantic to the site. Air masses arriving in any other sector are likely to have originated over the United Kingdom or Europe.[36]

At Mace Head even 'clean' air that typically arrives off the Atlantic from the west[36] contains higher 'background' concentrations of most gases than is found in baseline air at Cape Grim. During P2P 2006, methanol, acetone and acetaldehyde were 476 ppt, 118 ppt and <4 ppt, respectively, and represented 67% of the oxygenated VOCs measured.[14] In comparison, at Mace Head during NAMBLEX, methanol, acetone and acetaldehyde represented 85% of those oxygenated VOCs and measured 440 ppt, 500 ppt and 300 ppt, respectively.[40] So while methanol levels were similar at both sites, the levels of acetone and acetaldehyde were significantly higher at Mace Head.

CO at Cape Grim was 40 ppb for the majority of the campaign, except for one period of Melbourne influence and the Robbins Island bushfire. During NAMBLEX, CO was measured at 91.3 ppb in clean air.[36] Isoprene was measured at 14 ppt in baseline air at Cape Grim and at Mace Head isoprene has been found to range between 0.5 (below detection[36]) and 68 ppt.[41] DMS during P2P 2006 was 66 ppt, while during NAMBLEX at Mace Head DMS was 188 ± 112 ppt.[36] Both DMS and isoprene have been suggested as the precursors for new particle formation,[27,42] and it is clear that at Cape Grim the concentration of both precursor species is much lower than reported for Mace Head.

Table 1. A comparison between Cape Grim and Mace Head of the major atmospheric species, meteorological conditions and biology

	Cape Grim *Durvillaea potatorum*	Mace Head *Laminaria digitata*	Reference[A]
Biomass	82 kg m^{-2}	2.5 kg m^{-2}	[15],[52]
Extent of beds	Not known	Not known	
Iodine content	90 mg kg^{-1}	2500–50 000 mg kg^{-1}	[53],[7]
Iodine emission	18 pmol g^{-1} (FW) min^{-1}	4–130 pmol g^{-1} (FW) min^{-1}	[16],[33]
Ozone	15 ppb	35 ppb	[28],[43]
IO	0.5 ± 0.3 ppt (0.4)	1.2 ppt	This work [20],[20,22]
OIO	BDL (3 ppt)	10 ppt	[21],[22]
CH_2I_2	(BDL)	0.05 ppt	[26],[26]
CH_3I	2–6 (2) ppt	1–7 ppt	[15,24],[26]
Tidal range	±2 m	±6 m	This work [8]
OH	1–4 × 10^6 mol cm^{-3}	3–8 × 10^6 mol cm^{-3}	[44], [45,46]
NO_x (night/day)	4/12 ppt	67/78 ppt	[47],[48]
DMS	66 ± 32 ppt	188 ± 112 ppt	[14],[36]
Isoprene	14 ppt	0–68 ppt	[14],[36,41]
Methanol	476 ppt	440 ppt	[14],[40]
Acetone	118 ppt	500 ppt	[14],[40]
Acetyldehyde	<4 ppt	300 ppt	[14],[40]
CO	40 ppb	91.3 ppb	This work [36]
CH_4	1712 ± 2 ppb	1847 ± 12 ppb	[54],[54]
CO_2	377.92 ppm	369 ppm (2002)	This work [55]
Wind speed	8.7 ± 4.1 m s^{-1} (29.5 m s^{-1})	0.5–15 m s^{-1} (28 m s^{-1})	This work [36,37]
MBL height	1233 ± 360 m	800 m	This work [37,56]
Temperature	15.4 ± 2.6°C	15.2 ± 13°C	This work [36]
Relative humidity	74.6 ± 12.2%	85.7 ± 8.7%	This work [36]
Clean air mass origin	Southern Ocean	North Atlantic	
Polluted air	Melbourne	Europe	

[A]Cape Grim references are detailed first and Mace Head second for each reference location.

The concentration of ozone, an important oxidant in the atmosphere, is much lower at Cape Grim (15 ppb) than Mace Head (35 ppb), respectively, in the summer.[28,43] In addition, lower OH concentrations were observed at Cape Grim (1–4 × 10^6 molecules cm^{-3} *v.* 3–8 × 10^6 molecules cm^{-3}) at Mace Head.[44–46] At Cape Grim, the production of the OH radical in baseline air is dominated by photolytic conversion of ozone,[44] since Cape Grim is a low NO_x and VOC environment,[47] with NO_x in baseline air measured at 4/12 ppt (night/day). Sources of NO_x at Cape Grim are dominated by the oceanic source of NO,[47] while background sources of NO_x at Mace Head are dominated by destruction of peroxyacetyl nitrate,[48] which is related to anthropogenic sources and has a level of 67/78 ppt (night/day) in 'clean' onshore air.[48]

The levels of the major atmospheric species in air masses defined as clean for both Cape Grim and Mace Head are very different, thus affecting the production of secondary organic aerosol and modifying the sinks of other atmospheric species at each site. Hence the lifetimes and reaction paths of many species, including those of iodine and iodated species, differ between the two sites.

At Cape Grim the levels of all the iodated species thought to be critical (IO, OIO and CH_2I_2) in new particle formation at Mace Head were significantly lower than observed at Mace Head. OIO and CH_2I_2 were below detection limits. CH_3I was the only iodated species that showed higher levels at Cape Grim than at Mace Head. Atmospheric iodine was not monitored during P2P 2006, but given the differences in the major iodine carrying atmospheric species, the atmospheric chemistry of iodine at Cape Grim could be expected to differ to that observed at Mace Head. The nucleation events at Mace Head are the result of either iodine emissions from *Laminaria digitata* or from the production of iodine via the destruction of IO, in turn the result of reactions involving other iodated species such as CH_2I_2 emitted from the kelp.[15,6]

The lifetimes of I_2, IO, OIO and CH_2I_2 at Mace Head range from seconds to hours.[18,26] At Cape Grim only a lifetime of ~20 min for IO has been reported.[20] This longer lifetime reflects the very different atmospheric chemistry at Cape Grim and the dominance of clouds, reducing photolysis.[49,50] At Cape Grim, CH_3I has a lifetime of 4–5 days[25] and at Mace Head a lifetime of 1–3 days,[51] so at both the sites the potential for CH_3I to be involved in 'bursts' of new particles is limited. However, CH_3I will represent a source of IO and iodine at both locations.

Conclusion

During P2P 2006, precursor gases, such as IO and OIO, were close to or below detection limits. DMS and CH_3I measured at Cape Grim were at background levels and showed no spikes. However, CH_3I concentrations determined at the surface of the ocean did show more variation and some local spikes, one of which coincided with a peak in new particles at the Station.

Apart from one potential event on 11 February, no unambiguous new particle events were observed either at the Cape Grim Station or on the beach below, nearer the expected source of precursor gases. Post-frontal events were not observed and the only new particle formation and growth observed during the campaign was the result of the interaction of a bushfire plume with marine air.

The kelp *Durvillaea potatorum*, found at Cape Grim, is not a major source of new particles, but could still represent an important source of methyl iodide and iodine, which would have a role in local atmospheric chemistry.

Clearly, the processes identified at Mace Head where emissions from the local kelp *Laminaria digitata* contribute significantly to nucleation events, are not applicable at Cape Grim. This suggests that the role of macroalgae in providing the initiating precursors to particle formation is highly localised and species specific. Further work will be needed to assess a variety of locations in both the Northern and Southern Hemisphere to better understand how the processes at Mace Head might contribute globally to new particle formation.

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Appendix 4. Butler* et al. *2007

IODINE CYCLING IN THE ECOSPHERE, AND ITS RELEVANCE TO TASMANIA

Edward CV Butler, Michael R Grose, Clive F Burrett, Michael Pook and Richard Doyle

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